2007

Verification Of Pilot-scale Iron Release Models

Stephen Glatthorn
University of Central Florida

VERIFICATION OF PILOT-SCALE IRON RELEASE MODELS

by

STEPHEN PETER GLATTHORN
B.S. University of Central Florida, 2005

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Civil and Environmental Engineering
in the College of Engineering and Computer Science
at the University of Central Florida
Orlando, Florida

Spring Term
2007

Major Professors: John D. Dietz
James S. Taylor

ABSTRACT

A model for the prediction of color release from a pilot distribution system was created in 2003 by Imran. This model allows prediction of the release of color from aged cast iron and galvanized steel pipes as a function of water quality and hydraulic residence time. Color was used as a surrogate measurement for iron, which exhibited a strong linear correlation. An anomaly of this model was an absence of a term to account for pH, due to the influent water being well stabilized. A new study was completed to evaluate the effectiveness of corrosion inhibitors against traditional adjustment. Two control lines were supplied with nearly same water qualities, one at pH close to pHs and one at pH well above pHs. The resulting data showed that effluent iron values were typically greater in the line with lower pH. The non-linear color model by Imran shows good agreement when the LSI was largely positive, but underpredicted the color release from the lower LSI line. A modification to the Larson Ratio proposed by Imran was able to give a reasonable agreement to the data at lower LSI values. LSI showed no definite relation to iron release, although a visual trend of higher LSI mitigating iron release can be seen.

An iron flux model was also developed on the same pilot system by Mutoti. This model was based on a steady state mass balance of iron in a pipe. The constants for the model were empirically derived from experiments at different hydraulic conditions with a

constant water quality. Experiments were assumed to reach steady state at 3 pipe volumes due to the near constant effluent turbidity achieved at this point. The model proposes that the iron flux under laminar flow conditions is constant, while the iron flux is linearly related to the Reynolds Number under turbulent conditions. This model incorporates the color release models developed by Imran to calculate flux values from different water qualities. A limited number of experiments were performed in the current study using desalinated and ground water sources at Reynolds Numbers ranging from 50 to 200. The results of these limited experiments showed that the iron flux for cast iron pipe was approximately one-half of the predicted values from Mutoti. This discrepancy may be caused by the more extensive flushing of the pipes performed on the current experiments which allowed attainment of a true steady state. Model changes were proposed to distinguish between near stagnant flow and the upper laminar region, with the upper laminar region showing a slight linear increase.

Predictions using the galvanized flux model were not accurate due to an inferior color release model that was developed for galvanized pipes. The model exhibits a high dependence on sulfate concentrations, but concentrations of sulfates in the current experiments were low. This led to low predicted flux values when the actual data showed otherwise. A new galvanized model was developed from a combination of data from the original and current experiments. The predicted flux values using the new model showed great improvement over the old model, but the new model database was limited and the resulting model was not able to be independently tested.

Dedicated to my parents Gina and Jim Glatthorn, my grandmother Mary, my Aunt Gloria, and my cousin Nick, for their unwavering love and support that has allowed me to have come this far.

ACKNOWLEDGMENTS

I would like to thank Dr. John D. Dietz for chairing my advisory committee and offering invaluable help in analyzing the data generated for this thesis. His guidance and extensive expertise are the foundations of this document. Thanks are also due to my other committee members, Dr. James S. Taylor and Dr. Andrew A. Randall for their support on this project and in furthering my education. I would also like to thank Dr. Charles D. Norris for his expertise in the analytical work of this project.

I would like to thank the entire TBW project team, Abdulrahman Alshehri, Jorge Arevalo, Mukesh Choudhary, Xiaotao Guan, Phillip Lintereur, Xiaoli Liu, David MacNevin, Debraj Mukherjee, Avinash Shekhar, Erica Stone, Chandler Wilson, Rajendra Vaidya, Mingda Zhang, and Bingjie Zhao. The combined efforts of everyone allowed for the completion of this extensive project and the help all of you have given me I deeply appreciate.

I would like to also like to recognize the contributions of Oswald Wiesner and Dennis Marshall for their help in all areas of site work. I would also like to thank the University of Central Florida, the UCF Civil and Environmental Engineering Department, AWWARF and Tampa Bay Water for their financial support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Abbreviations	Meaning
Δ	Delta (calculated from the effluent value – influent value)
ALK	Represents Alkalinity in mg/L as Calcium Carbonate
ANOVA	Analysis of Variance
AWWARF	American Water Works Association Research Foundation
C	Apparent Color
Ca	Chemical Symbol for Calcium
$CaCO_3$	Chemical Symbol for Calcium Carbonate
CO_3^{-2}	Chemical Symbol for Carbonate
Cl^-	Chemical Symbol For Chloride
Cl_2	Chemical Symbol For Chlorine
COND	Represents the Conductivity of Water (in micro Siemens/cm)
CPU	Cobalt Platinum Units (unit of measuring color in water)
DO	Dissolved Oxygen
USEPA or EPA	Environmental Protection Agency
FCl_2	Represents a Free Chlorine Residual
Fe	Chemical Symbol for Iron
G	Galvanized Steel Pipe

Abbreviations	Meaning
GW	Ground Water
HCO_3^-	Chemical Symbol for Bicarbonate
HPC	Heterotrophic Plate Count
HRT	Hydraulic Residence Time
Km	Term Denoting Iron Flux (in mg of iron per square meter per day)
LCI or CICL	Lined Cast Iron Pipe
LI or LSI	Langelier Saturation Index
m	Meter (1m ≈ 3.28 feet)
Max	Denotes the Maximum Value of a Data Set
meq	Milliequivalent
	(molecular weight normalized by valence charge)
Min	Denotes the Minimum Value of a Data Set
Na^+	Chemical Symbol For Sodium
NTU	Nephelometric Turbidity Units
	(unit of measuring turbidity in water)
P	Chemical Symbol for Phosphorous
PDS	Pilot Distribution System
pH	The negative log of the hydrogen ion concentration (-log $[H^+]$)
PO_4^{-3}	Chemical Symbol for Phosphate
PVC	Polyvinyl Chloride Pipe
QA/QC	Quality Assurance-Quality Control

Abbreviations	Meaning
RO	Desalinated Water
Si	Silica (reported as mg/L of SiO_2)
SO_4^{-2}	Chemical Symbol For Sulfate
SW	Surface Water
TBW	Tampa Bay Water (the participating utility in this study)
TBWI	Refers to the previous research project: Effects of Blending on Distribution System Water Quality
TBWII	Refers to the current research project: Control of Distribution System Water Quality in a Changing Water Quality Environment Using Inhibitors
TCl_2	Indicates a combined chlorine residual
UCI or CI	Unlined Cast Iron Pipe
XPS	X-ray Photoelectron Spectroscopy

1 INTRODUCTION

1.1 Problem Description

One of the most pressing problems facing potable water utilities today is maintaining an acceptable water quality as the water passes through the distribution system. Guidelines for acceptable treated water quality are enforceable by law, which means that utilities must safeguard their water supplies against contamination or they could face monetary and legal consequences. Utilities can often make changes to their treatment facilities in order to achieve treatment regulations, but face enormous challenges if the water quality is mainly deteriorated by the distribution system itself. In most cases, replacing aged and broken pipe segments is a very expensive undertaking. Identifying areas where significant water quality deterioration takes place and deciding on acceptable solutions may be difficult as well. Distribution systems for some facilities may be very diverse in pipe size and material, which can lead to complications in determining an effective corrosion control strategy.

Some pipe materials, especially metallic materials such as iron or copper, can be corroded by water and release undesired by-products into the water stream. Problems resulting from corrosion are numerous, and can in extreme cases result in clogging and possible breakage of pipes. Corrosion in distribution system pipes is not a fully

understood process and is influenced by many factors that can make corrosion problems more severe in select locations. Currently accepted corrosion theories demonstrate a molecular scale of the chemical and physical changes the pipe surface undergoes, but over time the corrosion of the pipe material evolves into a layer of scale on the inside of the pipe. Corrosion indices have been developed from field and lab studies with the intent of producing a simplified relationship to predict corrosion. These indices are sometimes inadequate in determining corrosion potential and are frequently misused as universal corrosion predictors.

Sites of excessive corrosion can harbor microbiological contaminants that could possibly cause illness if released into the bulk stream and ultimately come into contact with someone. Corrosion can also affect aesthetic qualities by making the water appear colored or turbid, and can impart a metallic taste to the water. These reasons provide most utilities enough motivation to invest resources in evaluating corrosion control for their specific distribution system.

1.2 Research Objectives

The University of Central Florida has conducted a tailored collaboration project to evaluate control opportunities for distribution system water quality in a changing water quality environment using inhibitors. This project follows a related project performed from 2002-2004 entitled *Effects of Blending on Distribution System Water Quality.* Much of the work performed on the previous project lays the foundations of the research performed on the current project. The participating utilities include Tampa Bay Water

(TBW) and its subsidiary member governments of Pinellas, Hillsborough and Pasco Counties and the Cities of New Port Richey, St. Petersburg, and Tampa. Contributions have also been made to this project by the American Water Works Association Research Foundation (AWWARF). This multi-year project encompasses a wide range of work, of which this thesis incorporates some of that data. An upcoming overall report entitled *Control of Distribution System Water Quality in a Changing Water Quality Environment Using Inhibitors* will provide full details of all work performed on the current project.

The goals of this research project were to evaluate four commonly used corrosion inhibitors in a pilot distribution system and the effects they have on the release of corrosion products. Influent source water composition was varied at different intervals of the project, while inhibitor type and dose were kept constant in selected pipelines to allow for comparisons between inhibitors to be made. Samples taken from the pilot plant were analyzed for many water quality parameters on a regular basis to determine their effects on the release of metals and microbiological contaminants. Additional studies on corrosion involving electrochemical noise and pipe coupons for biological growth and surface roughness were also performed.

1.3 Thesis Objectives

The main goals of this thesis are to verify two iron release models developed in the TBWI project. The first objective was to evaluate a non-linear model that predicts color release from the pilot distribution systems. Apparent color measurements showed a strong correlation to iron, and were used as a surrogate measurement that is more

amenable to field testing. This model predicts color release as a function of many common water quality parameters. Evaluation of this model was based on data collected from two pipelines with no added corrosion inhibitor which were operated throughout the project. These lines were operated at different pH values to further examine the effects of pH and LSI on iron release.

The second model proposes that iron flux from aged pipes under laminar flow conditions is constant. In these studies, iron release was mainly in particulate form. This implied that the iron release was attributed to the removal of corrosion scales from the interior pipe surface. The model related the release of the corrosion products to the pipe geometry and hydraulic residence time. Experiments using a specific water quality over a wide range of flow rates (Reynolds numbers) for cast iron and galvanized steel pipes was used to empirically calibrate the model. The model is adapted for different water quality by relating the predicted color release from the current water quality to the predicted color release of the water used during the original experiments. Limited testing at laminar conditions on the cast iron and galvanized steel pipelines was performed to verify this model.

2 LITERATURE REVIEW

2.1 Introduction

The main goal of a water treatment facility is to provide clean and safe water to all consumers. Treatment processes vary among different facilities in the United States, but all treated water must meet a minimum level of requirements set forth by the EPA under the Safe Drinking Water Act (USEPA 2003). These standards were made in order to protect the public against harmful contaminants that can affect the public in a negative way. Many different compounds are regulated, including metals, organic and inorganic compounds, microorganisms, radioactive materials and disinfection by-products. Other contaminants that are not deemed harmful, but can have negative aesthetic qualities are listed as secondary contaminants. The secondary contaminants are not regulated, but suggested maximum levels have been established to avoid consumer complaints about unpleasant water.

Even if the finished water produced from a plant might meet all federal requirements, the quality of the water may deteriorate in the distribution system. Depending on piping material, undesired additives such as metals, particulates, and microorganisms may be released into the water under certain circumstances. These products result from the interactions of water with iron, copper, and lead pipes that allow corrosion to take place.

While copper and lead are regulated contaminants that are known to cause long-term health effects, iron is not known to have any significant detrimental health effects and is an essential nutrient to the human body. Iron is listed as a secondary standard, with a suggested concentration limit of 0.3 mg/L (USEPA 2003), because of the metallic taste and reddish color it imparts to water. Controlling iron release is still a priority, due to the damaging effects it can have in staining clothes and bathroom fixtures. A survey of the 100 largest AWWARF participating utilities found that the most frequently listed complaints stem from the corrosion of cast iron pipes (McNeil and Edwards 2001).

Other problems can arise from the formation of large iron tubercules on the inside pipe walls. These tubercules can become so large that they can severely reduce the flow capacity of the pipe (Curry 1978). The maintenance of distribution systems is also an expensive undertaking, and the premature deterioration of pipes can result in additional costs. The EPA estimates that a typical utility distribution system comprises the majority of capital costs, and that the replacement cost of distribution systems nationwide is well into the billions of dollars (Mullen and Ritter 1980). For these reasons it is in the best interest of a utility to contain iron release outbreaks with preliminary treatment measures before the finished water is allowed to enter the distribution system.

2.2 Iron Corrosion Mechanisms

Iron release from cast iron and galvanized pipes occurs because of corrosion. Corrosion is a process in which a metal is oxidized by the environment around it. Corrosion can occur by several mechanisms resulting from extreme temperatures, acidified

environments, corrosive soils, connections of dissimilar pipe materials, and physical stresses (Holler 1974). Other forms of corrosion are directly influenced by the water quality and flow conditions inside the pipe. Internal iron pipe corrosion can occur because the finished water has an oxidizing potential due to presence of dissolved oxygen. Finished waters generally have sufficient dissolved oxygen concentrations to promote corrosion due to aeration processes and natural equilibrium with the atmosphere. The theorized corrosion reactions of iron are shown as Equations 2-1 through 2-4, which were developed by Butler and Ison (1966) as an electrochemical cell with a reaction at the anode and a reaction at the cathode. The formed iron and hydroxide ions can then react to form a precipitate that can be released into the water.

$$2Fe \rightarrow 2Fe^{+2} + 4e^{-} \quad (2\text{-}1)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (2\text{-}2)$$

$$2Fe^{+2} + 4OH^{-} \rightarrow 2Fe(OH)_2 \quad (2\text{-}3)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad (2\text{-}4)$$

These reactions represent the corrosion process on a molecular scale. Over time, these reactions can be replicated, creating an iron scale that would coat the interior of the pipe. The naturally occurring scale will inhibit these corrosion reactions by resisting the flow of electrons (e^-) that fuels these electrochemical reactions. Pipe scales can become dislodged and release into the bulk stream from changes in flow patterns or changes in water quality. Other oxide forms, such as $FeCO_3$, FeOOH, Fe_2CO_3 and Fe_3O_4 can exist

in the iron scale and are formed following similar reactions to those in Equations 2-1 thru 2-4. In a study using X-ray Photoelectron Spectroscopy (XPS) on cast iron pipe segments, results showed the existence of these and other scales after exposure different blended water qualities (Tang et al. 2005). Sarin et al. (2004) also reported similar findings using XPS analysis on cast iron pipe segments from two different distribution systems. The types of scales that are formed are dependent on the localized environment at the corrosion sites, which is influenced by water quality and thermodynamic equilibrium. Each scale compound has unique physical properties which influence the tendency to be released from the pipe surface.

2.3 Commonly Accepted Methods to Iron Corrosion Control

Many methods have been utilized to mitigate iron corrosion in distribution systems based on research and pilot studies. The most common method involves the production of finished water that has potential to precipitate calcium carbonate ($CaCO_3$). Calcium and carbonate species are typically found in natural waters, and these compounds can precipitate into a solid form under favorable conditions. The precipitation of a thin layer of calcium carbonate inside the pipe will theoretically form a thin coat around the interior pipe surface that will protect the pipe surface from the cathodic/anodic reactions of the corrosion cell. If water quality conditions favor the potential to precipitate $CaCO_3$, the water is commonly referred as having a positive Langelier Saturation Index (LSI) (Langelier 1936). The LSI relates the pH of the water to the pH at which calcium carbonate is saturated in solution, which implies whether the water will precipitate or dissolve solid $CaCO_3$. The LSI does not account for the degree or amount of

precipitation, only if there is a tendency for precipitation to occur. LSI is defined in a simplified form by Snoeyink and Jenkins (1980).

$$LSI = pH - pHs \tag{2-5}$$

Where:

pH is the measured pH of the solution

pHs is the $CaCO_3$ saturation pH of the water, obtained from Equation (2-6)

$$pHs = pK_A - pK_{SO} + pCa - pHCO_3 - \log\gamma_{Ca} - \log\gamma_{HCO3} \tag{2-6}$$

Where:

pK_A is the log of the equilibrium constant for the bicarbonate-carbonate species

pK_{SO} is the solubility product constant for calcium carbonate ($CaCO_3$)

pCa is the log of the molar concentration of calcium in solution

$pHCO_3$ is the log of the molar concentration of bicarbonate in solution

γ is the activity coefficients (for both calcium and bicarbonate)

LSI is a common index used by engineers to refer to the corrosivity of the water, where a positive value of LSI is accepted to represent non-corrosive water. It is common for utilities to elevate the pH in order to obtain a positive LSI in the finished water. While LSI is a simplified way of dealing with corrosion problems, the measures of producing finished water with a positive LSI may or may not contribute to solving corrosion problems (McNeil and Edwards 2001). Rossum (1987) investigated many scrap iron pipes taken out of many distribution systems and found no calcium carbonate films

deposited on the interior pipe surfaces that had been supplied with positive LSI water. After investigating red water complaints for many utilities, he found that the complaints were minimized when the feed water had an LSI near zero. Pisigan and Singley (1985) conducted corrosion studies on galvanized steel pipes. Their results showed no distinct decrease in corrosion rates at positive LSI conditions when compared to tests using negative LSI waters. Mullen and Ritter (1980) researched the colored water complaints of the Middlesex Water Company in New Jersey. They discovered that after the utility started blending surface and ground waters, the utility still had numerous red water complaints even when the finished water was raised to LSI values greater than +0.5 units.

Other corrosion indices have been created based on lab or pilot scale studies. Other common indices such as the Aggressiveness Index, Ryznar Index, and the Calcium Carbonate Precipitation Potential are similar to the LSI. These indices attempt to improve upon the basic function of the LSI index by incorporating pH, calcium hardness, and alkalinity in different mathematical relationships. Studies have noted the strong correlations most indices have with the LSI, and how they give similar results (Imran, 2005a; Rossum and Merrill, 1980). Other indices incorporate different water quality parameters that have resulted in better correlations with some corrosion studies. The main problem with all indices stems from incorrect application. Many corrosion indices are not universal corrosion predictors that can be applied to all situations, but they are frequently used in this context. These indices should only be used as one factor as part of an overall corrosion assessment of a specific distribution system.

Alkalinity addition has also been shown to help mitigate the problems of iron release. The addition of alkalinity has been reported to help reduce iron release and corrosion rates (McNeil and Edwards, 2001), but the addition of alkalinity may have a detrimental effect in increasing copper release. A tradeoff might exist for utilities if alkalinity supplementation is used. Edwards et al. (1996) conducted a study on the feasibility of commonly accepted corrosion reduction methods. They concluded that increased bicarbonate alkalinity in the finished water increased copper concentrations in a near linear relationship. Direct alkalinity supplementation with sodium bicarbonate inherently includes an addition of sodium, which raises conductivity and TDS levels that can have a negative effect on iron release (Shull 1980). Alkalinity can also be added through recarbonation using lime ($Ca(OH)_2$) which avoids the addition of sodium, but this process is more expensive. Based on these findings, supplementation of alkalinity can be a double edged sword as a corrosion inhibitor.

2.4 Effects of Water Quality on Iron Release

The quality of the water in many ways is the cause of iron release from cast iron and galvanized pipes. Many studies have investigated the effects different water quality has on distribution system corrosion. The results of these studies are not always consistent, as different conditions can drastically change the extent of corrosion without respect to a singular parameter. The follow discussion summarizes some studies that investigated the roles that some water quality parameters have on corrosion.

2.4.1 pH and Alkalinity

The parameters of pH and alkalinity are related in calcium carbonate solubility, and are generally the two main parameters that are considered to reduce iron corrosion if increased. Addition of basic chemicals, such as sodium hydroxide (NaOH), will raise the pH as well as the alkalinity. Correspondingly, the separation of the effects of pH from the effects of alkalinity in corrosion studies is difficult. Sarin et al. (2003) concluded that increasing the pH from 7.6 to 9.5 reduced the amount of iron released to water in a pilot cast iron distribution system. Low iron levels were reached only after a few months of equilibration at these high pH levels. The study also noted that the influent water supplied to this cast iron pipe was relatively low in alkalinity (<60 mg/L as CaCO3), and that significant increases in alkalinity were found to have benefit in reducing iron release. Alkalinity is also known for increasing buffer intensity, which has also been found to be effective in combating iron corrosion (McNeil and Edwards, 2001).

2.4.2 Temperature and Dissolved Oxygen

Temperature has a large effect on most chemical and biological reactions. Thus it can significantly impact corrosion in many indirect ways. pH, solubility, and dissolved oxygen concentrations in water are influenced by temperature. Control of water temperature in the distribution system is not a feasible option, which requires many corrosion control strategies to be adapted depending on seasonal temperatures.

Studies by Volk et al. (2000) reported that temperature has a strong relationship with corrosion rates, and that corrosion control strategies should be changed seasonally. They

reported that the maximum corrosion rate obtained in the summer was seven times greater than the minimum corrosion rate obtained in the winter. This research was conducted on annular reactors constructed of cast iron pipe using actual finished water from a utility that practiced corrosion control by dosing zinc orthophosphate.

Dissolved oxygen (DO) can be at near saturation levels before entering some distribution systems. Based on the Butler and Ison corrosion reactions, these high dissolved oxygen concentrations should significantly fuel the corrosion process. In actual systems, the effects of dissolved oxygen can change depending on the oxygen concentration and other external characteristics. In stagnant conditions, evidence exists that dissolved oxygen may benefit in preventing iron release by helping to form more stable iron scales (Sarin et al 2004). This benefit may be offset by findings that demonstrate the ability of dissolved oxygen to increase corrosion rates and tuberculation (McNeil and Edwards 2001). Studies by Pisigan and Singley (1985) have seen higher corrosion rates and iron release under higher DO concentrations in galvanized pipes. In their study, greater corrosion rates of galvanized pipes occurred when DO concentrations were 9 mg/L then when concentrations were 5 mg/L. These results occurred at positive and negative LSI values. These findings support the complex relationship dissolved oxygen has on pipe corrosion. Utilities would have difficulty in classifying pipe scale and hydraulic conditions in all sections of their distribution system. Without a full distribution system examination, the effects of dissolved oxygen on iron release cannot be fully predicted, and the utility would need to rely on the limited information it can feasibly collect.

2.4.3 Dissolved Solids

Dissolved solids are always present in natural waters, and are commonly added as byproducts during chemical treatment. Common dissolved solids in waters are calcium, sodium, chlorides, sulfates, and bicarbonate, with others present in varying quantities depending on source. Butler and Ison (1966) separated the effects of dissolved solids into "aggressive" ions that attack iron scales, and "passive" ions that help form stable scales. Chlorides and sulfates are generally considered to be aggressive ions that are incorporated into corrosion indices such as the Larson ratio and the FGY index (Larson and Skold 1958, Feigenbaum 1978). Many of these indices were developed due to inadequate correlations between LSI and iron release in waters containing high dissolved solids concentrations. Other studies have refuted the effects of chlorides and sulfates on disturbing iron scales under certain conditions. Piron et al (1986) reported that chlorides and sulfates had no correlation to weight loss in cast iron pipe. A study by Bondietti et al. (1993) reported the evidence of sulfate reducing the dissolution of iron oxides on cast iron pipe. A general consensus seems to support that increased amounts of chlorides and sulfates have some effect on iron scales, even if the effects might vary under different conditions.

2.5 Biological Effects on Iron Release

The effects of microbiological organisms on iron release can also be significant. Bacterial populations can thrive inside pipe scales that can shield them from residual disinfectants in the bulk stream. Emde et al (1992) reported that a heterogeneous population of potentially corrosive microorganisms was present in treated water and

corrosion tubercles. This population included iron reducing and iron precipitating bacteria even at low temperatures (0^{o}C). Studies by Volk et al. (2000) reported that metal oxide films provide a haven for iron-oxidizing bacteria that can influence the solubility of iron.

Frateur et al. (1999) also reported that the corrosion of cast iron has a negative impact on maintaining free chlorine residual in the distribution system. With a loss of residual, biological growth can occur in the system and lead to overgrowth of the biofilm and possible illness outbreaks. Broo et al. (1999) found that the corrosion rate of iron decreases in the presence of natural organic matter. They attribute the results of their study to complexation between the organic matter and the iron surface.

2.6 Effect of Phosphate and Silicate Inhibitors on Iron Release

Corrosion inhibitor use becomes more popular each year, as an increasing amount of utilities seek to improve distribution system water quality. McNeil and Edwards (2002) conducted a study of participating utilities to analyze trends of inhibitor use. Their findings show that utilities switch to corrosion inhibitors for many reasons, with the most common reason to meet lead and copper regulations. The report also finds that many utilities have success using inhibitors, but under certain conditions inhibitors can make problems worse. This leads to conflicting reports about the effects of inhibitor use in pilot and lab studies.

McNeil and Edwards (2000) also conducted a four-year study on iron release from cast iron pipes under stagnant water conditions with phosphate based inhibitor. Their conclusions stated that the addition of phosphate inhibitors produced no beneficial effect in reducing iron release in most experiments and some experiments actually showed increased iron release.

Volk et al. (2000) found that an increased zinc orthophosphate dosing during months with elevated temperatures reduced corrosion rates to an acceptable value in an iron water main. The authors cautioned that corrosion rates can reach elevated levels during high seasonal temperatures, despite the addition of corrosion inhibitor. Rushing et al. (2003) reported that increasing doses of silicate inhibitor into a cast iron pipe resulted in increased iron release and tuberculation. The iron films on the interior pipe surface changed structure after the 4 month study, and the released iron particulates were smaller in size.

Appenzeller et al. (2001) reported that phosphate treatment of highly corroded cast iron pipe had a positive effect. They reported that phosphate inhibitor reduced the release of iron oxides and limited the proliferation of heterotrophic bacteria in pipes by modifying the properties of the corrosion products. Experiments on slightly corroded steel pipes were only moderately effective in controlling the same aspects.

The utility serving Carbondale, Illinois switched from using caustic soda (NaOH) to zinc phosphate to control corrosion (Swayze 1983). The plant produced relatively soft water

which required a large dose of caustic to reach a positive LSI. The zinc phosphate concentration used by the utility was significantly less than the caustic dose, which resulted in significant cost savings. Consumer complaints about red water dropped significantly after inhibitor use had begun, with a subsequent decline in water main tuberculation.

Use of a zinc orthophosphate inhibitor in Boston, Massachusetts showed little reduction in the release of lead and copper from aged distribution pipes (Karalekas et al. 1983). The addition of sodium hydroxide to the relatively soft water and resulting increase in pH was shown to be effective in reducing the lead and copper levels. Some reduction in iron levels was also seen as a result of this treatment, although the main focus was the reduction of lead and copper to regulated levels. Other studies have generally found that inhibitor use has a greater effect on lead and copper release than on iron release.

2.7 Review of Work Performed in TBW I

In the first TBW project, an iron release model and an iron flux model were developed by Imran (2005) and Mutoti (2007), respectively. The models were based on the same pilot distribution system that was used for this study. In TBW I, 14 hybrid pipelines lines were constructed of 4 common piping materials (unlined cast iron, lined cast iron, polyvinyl chloride, and galvanized steel). These lines were fed with different blends of treated source waters. These blends were composed of vastly different water qualities, which allowed for the development of a comprehensive iron release model based on water quality. The pilot distribution system also incorporated four lines constructed of a single

material to evaluate the effects of pipe material on effluent water quality. Isolated experiments were performed to examine iron release from unlined cast iron and galvanized pipes. The results of these experiments were used to develop an iron flux model based on pipe geometry and flow conditions.

Imran's (2005) color release model was based on average influent water quality of the 14 hybrid lines and incorporated 12 months of pilot plant data, and was tested using an independent set of data during separate experiments. The model displayed as Equation 2-7 shows that apparent color could be closely predicted based on the influent water quality parameters of sodium, chlorides, sulfates, dissolved oxygen, temperature, alkalinity, and hydraulic residence time in the pipe. This model closely predicted (R^2 = 0.83) actual color values recorded in the field.

$$\Delta C = \frac{(Cl^-)^{0.485} \times (Na^+)^{0.561} \times (SO_4^{-2})^{0.118} \times (DO)^{0.967} \times (T)^{0.813} * (HRT)^{0.836}}{20.7 \times (ALK)^{0.912}} \qquad (2\text{-}7)$$

Where:

ΔC is the change in apparent color: effluent – influent (CPU)

Cl^- is the chloride concentration (mg/L)

Na^+ is the sodium concentration (mg/L)

SO_4^{-2} is the sulfate concentration (mg/L)

DO is the dissolved oxygen concentration (mg/L)

T is the temperature (°C)

HRT is the hydraulic residence time (days)

ALK is the alkalinity (expressed as mg/L $CaCO_3$)

A model predicting the color release from galvanized pipe was also created from data gathered on the line constructed only of galvanized pipe. The model incorporated a smaller data set and differs slightly from the hybrid model. Equation 2-8 shows the developed model for the prediction of color release from galvanized pipe.

$$\Delta C = 10.71 \times (ALK)^{-1.62} \times (Si)^{-0.55} \times (SO_4^{-2})^{1.12} \times (T)^{1.06} \quad (2\text{-}8)$$

Where:

ALK is the alkalinity (expressed as mg/L $CaCO_3$)

SO_4^{-2} is the sulfate concentration (mg/L)

Si is the silicate concentration (expressed as mg/L SiO_2)

T is the temperature (°C)

Furthermore, apparent color values were found to have a linear relationship with effluent iron concentrations (R^2 = 0.82). The linear relationship shows that iron and color are interrelated in the pilot distribution system and that using color as a surrogate measurement for iron is valid.

$$\Delta Fe = 0.0132 \times (\Delta C) \quad (2\text{-}9)$$

Where:

ΔFe is change in iron concentration from influent to effluent in mg/L

The color release models do not incorporate pH, conductivity, calcium, and UV254 measurements because they were determined to be statistically insignificant using an analysis of variance (ANOVA) at the 95% confidence level. The omission of pH from the model may be appropriate for this data set because the waters were typically fed into the system with large (> +0.4) LSI values. A positive LSI value corresponds to a supersaturated solution with respect to $CaCO_3$, which is mentioned in many studies as a possible corrosion deterrent.

Imran et al. (2005a) also evaluated the LSI and other corrosion indices. The results showed that the LSI and other calcium carbonate based indices were not well correlated to iron release. One corrosion index which was found to correlate well with iron measurements in the first TBW project is the Larson Ratio. Empirically derived, the Larson Ratio incorporates the corrosive effects of chlorides and sulfates against the beneficial properties of alkalinity (Larson & Skold 1958). The Larson Ratio (LR) is presented as Equation 2-10.

$$LR = \frac{(Cl^- + SO_4^{-2})}{(HCO_3^-)} \qquad (2\text{-}10)$$

Where:

Cl^- is the equivalent concentration of chloride ion [meq/L]

HCO_3^- is the equivalent concentration of bicarbonate [meq/L]

SO_4^{2-} is the equivalent concentration of sulfate [meq/L]

Based on this work, Imran et al. (2005a) developed the Modified Larson Ratio (MLR) to account for temperature and hydraulic effects. Equation 2-11 shows the new relationship.

$$MLR = \frac{(Cl^- + SO_4^{-2} + Na^+)^{1/2} \times (T) \times (HRT)}{(25 \times ALK)} \quad (2\text{-}11)$$

Where:

Cl^- is the concentration of chlorides (mg/L)

SO_4^{2-} is the concentration of sulfate (mg/L)

Na^+ is the concentration of sodium (mg/L)

T is the temperature (^oC)

HRT is the hydraulic retention time (days)

ALK is the alkalinity of the sample (mg/L $CaCO_3$)

Iron flux models were developed by Mutoti et al. (2007) to predict the iron release under variant hydraulic conditions. The model was derived from a steady state mass balance of iron in the pipe. Based on pilot studies using aged pipes, the iron release was found to be mostly in the particulate form. This implies that the iron release from aged pipes is influenced more by the removal of iron scales than from direct corrosion of the pipe material. With this assumption, the iron release could be modeled as a mass of iron removed from the interior pipe surface area per time. Equation 2-12 shows the simplified equation which relates iron release to the hydraulic residence time and geometric properties of the pipe.

$$\Delta Fe = \frac{Km \times HRT}{4 \times D} \quad (2\text{-}12)$$

Where:

ΔFe is the change in iron concentration as it passes through the pipe (mg/L)

Km is the iron flux (mg of iron/meter^2-day)

HRT is the hydraulic residence time (days)

D is the diameter of the pipe (meters)

The model was developed under assumed steady state conditions after the effects of HRT on iron release were studied. These flux models were tested under laminar and turbulent flow conditions on the UCI and G PDS. It was found from the experiments that the iron flux under laminar flow conditions was approximately constant with respect to a constant water quality. The average flux values were 1.99 mg Fe/m^2-day for galvanized pipe, and 4.16 mg Fe/m^2-day for cast iron pipe. Under turbulent conditions, flux was found to be linearly related to the Reynolds Number. Calibrated models developed for turbulent conditions (Re >2000) are shown as Equations 2-13 and 2-14.

$$Galvanized\ Pipe: \quad Km = 4.5 \times 10^{-3}(\mathrm{Re} - 2000) + 1.99 \quad (2\text{-}13)$$

$$Cast\ Iron\ Pipe: \quad Km = 9.0 \times 10^{-3}(\mathrm{Re} - 2000) + 4.16 \quad (2\text{-}14)$$

Where:

Km is the iron flux (mg iron/m^2-day)

Re is the Reynolds Number, calculated by Equation 2-15:

$$\mathrm{Re} = \frac{DV}{\nu} \tag{2-15}$$

Where:

D is the pipe diameter (m)

V is the flow velocity (m/sec)

ν is the kinematic viscosity (m^2/sec)

(ν can be assumed to be $1x10^{-6}$ m^2/sec at ambient temperatures near 20°C)

This model was based on a constant water quality, as experiments were conducted using only one water composition (60% GW, 30%SW, 10% RO). The flux model was adapted to predict flux under variant water quality conditions by incorporating the Imran et al (2005) color release model. The adjustment term relates the predicted color of the influent water quality to the predicted water quality of the blend used during the experiments. Equation 2-16 shows the flux term being adjusted for water quality (Km_{adj}).

$$Km_{adj} = Km \times \frac{\Delta C_1}{\Delta C_2} \tag{2-16}$$

Where:

Km is the flux value (mg of iron/meter^2-day)

ΔC_1 is the predicted color of the influent water quality (CPU)

ΔC_2 is the predicted color of the blend used for experiments (CPU)

2.8 Summary

The main goals of this work are to verify two iron release models previously mentioned under a different experimental plan. Examination of the Imran et al (2005) color prediction model under variant pH conditions can expand on the original findings. The developed model has limited use in a practical aspect, as many utilities cannot operate at a highly positive LSI due to scaling issues. Experiments at laminar conditions with a different water quality can expand on the iron flux model developed by Mutoti et al (2007). Independent experiments can validate the original calibrations of these models under different water qualities. Experiments at low Reynolds numbers examine iron release at stagnant conditions, where it has been reported to be more severe.

2.9 References

1. Appenzeller, B. et al, 2001. Effect of Adding Phosphate to Drinking Water on Bacterial Growth in Slightly and Highly Corroded Pipes. *Wat. Res*., 35:4:1100.
2. Broo, A.; Berghult, B.; and Hedberg, T., 1999. Drinking Water Distribution - The Effect of Natural Organic Matter on the Corrosion of Iron and Copper. *Wat. Sci. and Technol.*, 40:9:17.
3. Benefield L.; Judkins, J.; & Weand, B., 1980. *Process Chemistry for Water and Wastewater Treatment*, Prentice Hall, New Jersey.
4. Bondietti, G.; Sinniger, J.; & Stumm, W., 1993. The Reactivity of Fe(III) Oxides: Effects of Ligands in Inhibiting the Dissolution. *Colloids & Surfaces A: Physiochemical & Eng. Aspects,* 79:2-3:157
5. Butler, G. & Ison, H., 1966. *Corrosion and its Prevention in Waters*. Reinhold Publishing, New York.
6. Curry, M., 1978. Is Your Water Safe and What Difference Does It Make. *Jour. AWWA*, 70:9:506
7. Edwards, M.; Schock, M.; & Meyer, T., 1996. Alkalinity, pH and Copper Corrosion By-product Release. *Jour. AWWA,* 88:3:81.
8. Emde, K.; Smith, D.; & Facey, R., 1992. Initial Investigation of Microbially Influenced Corrosion in a Low Temperature Water Distribution System. *Wat. Res.*, 26:2:169.
9. Feigenbaum, C.; Gal-or, L.; & Yahalom, J., 1978. Scale Protection Criteria in Natural Waters. *Corrosion,* 34:4:133.

10. Frateur, I. et al, 1999. Free Chlorine Consumption Induced by Cast Iron Corrosion in Drinking Water Distribution Systems. *Wat. Res.*, 33:8:1781.
11. Holler, A., 1978. Corrosion of Water Pipes *Jour. AWWA*, 70:8:456.
12. Imran, S. et al, 2005. Red Water Release in Drinking Water Distribution Systems. *Jour. AWWA*, 97:9:93.
13. Imran, S. et al, 2005a. Modified Larsons Ratio Incorporating Temperature, Water Age, and Electroneutrality Effects on Red Water Release. *Jour. ASCE*, 131:11:1514.
14. Karalekas, P.; Ryan, C.; and Taylor, F., 1983. Control of Lead, Copper, and Iron Pipe Corrosion in Boston. *Jour. AWWA*, 75:2:92.
15. Langelier, W., 1936. The Analytical Control of Anti-Corrosion Water Treatment *Jour. AWWA,* 28:10:1500.
16. Larson, T. & Skold, R., 1958. Laboratory Studies Relating Mineral Water Quality of Water to Corrosion of Steel and Cast Iron. *Corrosion,* 14:6:43.
17. McNeill, L. & Edwards, M., 2002. Phosphate Inhibitor Use at U.S. Utilities. *Jour. AWWA*, 94:7:57.
18. McNeill, L. & Edwards, M., 2001. Iron Pipe Corrosion in Distribution Systems. *Jour. AWWA*, 91:7:93.
19. McNeill, L. & Edwards, M., 2000. Phosphate Inhibitors and Red Water in Stagnant Iron Pipes. *Jour. Env. Eng.*, 126:12:1096.
20. Mullen E. and Ritter J., Monitoring and Controlling Corrosion by Potable Water *Jour. AWWA,* 72:5:286.

21. Mutoti, G. et al, 2007. Development of a Novel Iron Release Flux Model for Distribution Systems. *Jour. AWWA*, 99:1:102.

22. Piron, D. et al, 1986. Corrosion Rate of Cast Iron and Copper Pipe by Drinkable Water. *Corrosion Monitoring in Industrial Plants Using Non-destructive Testing and Electrochemical Methods, ASTM STP 908.* American Society of Testing & Materials, Philadelphia.

23. Pisigan R. and Singley J., Effects of Water Quality Parameters on the Corrosion of Galvanized Steel. *Jour AWWA,* 77:11:76.

24. Price, S. & Jefferson, F., 1997. Corrosion Control Strategies for Changing Water Supplies in Tucson, Arizona. *Jour. N.E.W.W.A.*, 111:3:285.

25. Rossum, J., Dead Ends, Red Water and Scrap Piles. *Jour. AWWA*, 79:7:113.

26. Rushing, J.; McNeill, L. and Edwards, M., 2003. Some Effects of Aqueous Silica on the Corrosion of Iron. *Wat. Res.*, 37:5:1080.

27. Sarin P.; Snoeyink, V.; Lytle, D. & Kriven, W., 2003. Iron Release from Corroded, Unlined Cast Iron Pipe. *Jour. AWWA*, 95:11:85.

28. Sarin, P.; Snoeyink, V.; Lytle, D.; & Kriven, W., 2004. Iron Corrosion Scales: Model for Scale Growth, Iron Release, and Colored Water Formation. *Jour. Env. Eng.*, 130:4:364.

29. Shull, K., 1980. An Experimental Approach to Corrosion Control. *Jour. AWWA*, 72:5:280.

30. Swayze, J., 1983. Corrosion Study at Carbondale, Illinois. *Jour. AWWA*, 75:2:101.

31. Tang, Z. et al., 2005. Characteristics of Iron Corrosion Scales Established Under Blending of Ground, Surface and Saline Waters and Their Impacts on Iron Release in the Pipe Distribution System. *Corr. Sci.*, 48:2:322.
32. USEPA, 2003. National Primary Drinking Water Standards, Washington, D.C.
33. Volk, C.; Dundore, E.; Schiermann, J.; & LeChevallier M., 2000 Practical Evaluation of Iron Corrosion Control in a Drinking Water Distribution System. *Wat. Res.*, 34:6:1967.

3 METHODS AND MATERIALS

3.1 Site Description

During the first project, treated groundwater, surface water, and desalinated water were mixed in different proportions and fed into 14 hybrid pilot distribution systems (PDS). These pilot distribution systems consisted of unlined cast iron (CI), lined cast iron (LCI), polyvinyl chloride (PVC) and galvanized steel (G) sections which were designed to simulate actual distribution systems used by the TBW utilities. Actual distribution system pipes from the area were removed from service and used to construct these PDS. The setup of these hybrid lines was designed to be consistent configuration involving similar lengths of PVC, LCI, CI, and G pipes respectively. The hydraulic retention time was also kept constant for all PDS at two days.

In addition, the effluent water from the PDS were fed to loops of copper tubing containing lead coupons to simulate lead soldered home plumbing systems. These loops were flushed daily to simulate usage at a typical residence. Four additional PDS lines were also constructed, each containing a single pipe material. These lines allowed for experiments to test the effects of a singular pipe material on water quality. The PDS description is listed below with Figure 3-1 that illustrates the actual set-up of the pilot plant.

- PDS 1-14: Hybrid sections of PVC, LCI, UCI, and G pipe (approximately 90 feet)
- PDS 15: Eight sections of 6-inch diameter UCI pipe (approximate length 90 feet)
- PDS 16: Five sections of 6-inch diameter LCI pipe (approximate length 90 feet)
- PDS 17: Five sections of 6-inch diameter PVC pipe (approximate length 100 feet)
- PDS 18: Ten sections of 2-inch diameter G pipe (approximate length 140 feet)

Figure 3-1: PDS Layout and Copper Loops

3.2 Finished Water

The blend used for the influent in all 14 hybrid PDS lines was made each week from a certain percentage of groundwater, surface water, and desalinated water. Ground water came from the Cypress Creek Well Field; surface water was obtained from the TBW Regional Plant in Tampa. Desalinated water was prepared from ground water passed through a reverse osmosis membrane and sea salt chemicals were added to simulate desalinated water. Source waters were treated according to Table 3-1 and were prepared in weekly batches.

Table 3-1: Source Water Summary

Water Type	Treatment
Ground Water (GW)	Treatment by aeration, free chlorine, added ammonia to form combined chlorine.
Surface Water (SW)	Treatment by ferric sulfate coagulation, flocculation, settling, filtration, disinfection by ozonation, biologically activated carbon filtration, disinfection residual from combined chlorine.
Desalinated Water (RO)	Treatment by reverse osmosis membranes, aeration, disinfection by free chlorine, added ammonia to form combined chlorine, dissolved salt addition to simulate desalination product.

3.2.1 Phase Blend Composition

The entire project was broken down into four phases, which denoted a change in influent water blend. After each 3-month phase, the blend composition was changed to evaluate the water quality effects on inhibitor performance. Different percentages of each source water were used which allowed variations in water quality. Table 3-2 shows the blend composition by phase. This was designed to simulate actual production of TBW finished waters which would not be constant every day due to consumer demand. Following the completion of phases I, II, and III, a free chlorine burn was allowed for 1 week for bacteriological studies.

Table 3-2: Blend Composition by Phase

Phase	% GW in Blend	% SW in Blend	% RO in Blend
I (Feb – May 2006)	62	27	11
II (May - Aug 2006)	27	62	11
III (Aug – Nov 2006)	62	27	11
IV (Nov 2006 - Feb 2007)	40	40	20

3.3 New Modifications to Plant Operation

The overall goal of the TBW II project was to evaluate the effects of corrosion inhibitors under changing water qualities. Four corrosion inhibitors (blended ortho-phosphate, ortho-phosphate, zinc ortho-phosphate and silicate) were added to the influent blend in each phase of the 1-year project to evaluate the effects on metal release. Three target doses for each inhibitor were added to a separate PDS.

The project involved dosing 4 different inhibitors at 3 different concentrations into 12 pilot distribution systems (PDS). Two extra PDS lines (PDS 13 and 14) were supplied with control water with no added inhibitor. PDS 13 is supplied with the water near pHs (LSI = +0.3), and PDS 14 is supplied with water at a target pH well above pHs. These control lines allow for comparisons of traditional LSI corrosion control methods to dosing corrosion inhibitors.

3.3.1 Inhibitor Dosing

Dosing of inhibitors was performed by diluting the stock inhibitor solution in 55 gallon tanks to a specific concentration. The tank would feed three pumps that were calibrated to deliver a certain concentration into the influent standpipe. The inhibitor would mix with the blend flow before entering the PDS. New batches of inhibitor were made weekly using fresh blend water prepared that week. Figure 3-2 shows one of these inhibitor tanks and its configuration in the PDS system.

Figure 3-2: Picture of Inhibitor Tanks Dosing the PDS Lines

Dosing of inhibitor was kept constant for each PDS throughout the entire project. The first three lines received blended ortho-phosphate (BOP), PDS 4-6 received ortho-phosphate (OP), PDS 7-9 received zinc ortho-phosphate (ZOP), and PDS 10-12 received silicate (SiO2). The phosphate inhibitors were dosed as mg/L of phosphorous (P), while the silicate inhibitors were dosed as mg/L of silicate (SiO_2). Table 3-3 displays the targeted dosing scheme. Silica dosing was changed after the first few weeks of Phase I due to solubility problems in the inhibitor tank. Original dosing of 10, 20, and 40 mg/L was changed to the doses shown below for the rest of the project.

Table 3-3: Inhibitor Dosing Schedule

Inhibitor Type	**Low Dose**	**Medium Dose**	**High Dose**
BOP (PDS 1-3)	0.5 mg/L-P	1.0 mg/L-P	2.0 mg/L-P
OP (PDS 4-6)	0.5 mg/L-P	1.0 mg/L-P	2.0 mg/L-P
ZOP (PDS 7-9)	0.5 mg/L-P	1.0 mg/L-P	2.0 mg/L-P
SiO_2 (PDS10-12)*	3 mg/L-SiO_2	6 mg/L-SiO_2	12 mg/L-SiO_2

* Denotes dosing schedule used following the first few weeks of Phase I

3.3.2 Sampling Procedures

Sampling from the 14 PDS lines followed a schedule according to Table 3-4. Sampling was taken at the influent (I) and effluent (E) ports. Parameters that are denoted below were changed in frequency at the end of Phase I due to labor issues from weekly to biweekly for PDS 1-12.

Table 3-4: PDS Sampling Frequency

Parameter	**Sampling Frequency**	**Sample Points**	**Method of Quantification**
Ammonia	Weekly	I,E	Ammonia Probe
pH	Weekly	I,E	pH Probe
Alkalinity*	Weekly	I,E	Titration
Calcium*	Weekly	I,E	Titration/ICP
Magnesium*	Weekly	I,E	Titration/ICP
UV-254*	Weekly	I,E	Spectrophotometer
HPC	Weekly	I,E	Plate Count
Dissolved Oxygen*	Weekly	I,E	Dissolved Oxygen Meter
Temperature*	Weekly	I,E	Dissolved Oxygen Meter
NPDOC*	Weekly	I,E	TOC Analyzer
Nitrites	Weekly	E	Spectrophotometer
Silica	Weekly	I,E	Spectrophotometer/ICP
Total Chlorine	Weekly	I,E	Spectrophotometer
Free Chlorine	Weekly	I,E	Spectrophotometer
Turbidity*	Weekly	I,E	Spectrophotometer
Redox Potential*	Weekly	I,E	Platinum Electrode
Apparent Color*	Weekly	I,E	Spectrophotometer
Conductivity*	Weekly	I,E	Conductivity Probe
Ortho-Phosphate	Twice Weekly	I,E	Spectrophotometer
Total Phosphorous*	Weekly	I,E	ICP
Sodium*	Weekly	I,E	Spectrophotometer
Chloride*	Weekly	I,E	Titration/IC
Sulfate*	Weekly	I,E	Spectrophotometer/IC
Copper*	Weekly	I,E	ICP
Zinc*	Weekly	I,E	ICP
Total Lead*	Weekly	I,E	ICP
Total Iron*	Weekly	I,E	Spectrophotometer/ICP

*Frequency Change from Weekly to Biweekly beginning in Phase II (PDS 1-12)

3.3.3 Control Lines – PDS 13 and 14

During the entire project, PDS 13 and 14 were designated as control lines. These lines were fed with blend water at adjusted pH values and contained no corrosion inhibitor. PDS 14 was typically fed with water with LSI values of greater than +0.3, while PDS 13 was fed with the same blend that was adjusted to target an LSI less than +0.3. This was achieved through the addition of a small amount of hydrochloric acid to a separate tank containing blend water. This addition resulted in slight differences in influent water quality between PDS 13 and PDS 14. The most notable water quality differences resulted in increased chlorides and decreased alkalinity resulting from the acid addition. LSI was determined by the using a simplified form of the equation presented in Equation 3-1, which is as follows:

$$LSI = pH - pHs \tag{3-1}$$

pH_S determined by Equation 3-2:

$$pHs = K - log_{10}\left(\frac{Ca}{100{,}000}\right) - log_{10}\left(\frac{Alk}{50{,}000}\right) + 5A\left(\frac{\sqrt{I}}{I+\sqrt{I}} - 0.3I\right) \tag{3-2}$$

Where:

K and *A* are temperature dependent constants found in Table 3-5

Ca is the calcium concentration as $CaCO_3$

Alk is the alkalinity concentration as $CaCO_3$

I is the ionic strength

Table 3-5: Temperature Dependent Constants for LSI Calculations

Temperature (^{o}C)	K	A
5	2.16	0.494
10	2.08	0.498
15	2.00	0.502
20	1.93	0.506
25	1.85	0.511
30	1.78	0.515

The ionic strength may be approximated by Equation 3-3:

$$I = 1.6 \times 10^{-5} \times (COND) \tag{3-3}$$

Where:

$COND$ is the conductivity in micro Siemens/cm (μS/cm).

3.4 Flux Experiments

The experiments to analyze the iron flux model were performed on PDS 15, which was constructed of unlined cast iron pipe, and PDS 18 which was constructed of galvanized pipe. The iron release study was performed in conjunction with chlorine residual studies, which did not allow for complete independence of experimental design. Only GW and RO sources were used. Flow was adjusted to target Reynolds numbers between 50 and 200. Sample ports between each pipe length allowed for internal sampling. The approximate lengths of each pipe section in PDS 15 and PDS 18 are shown in Table 3-6.

Table 3-6: PDS Pipe Lengths

Pipe Section	PDS 15	PDS 18
1	12	13
2	12	15
3	12	13
4	12	21
5	11	25
6	11	7
7	10	20
8	11	20
9	--	10

* all lengths are in units of feet

3.4.1 PDS Operation

Influent water to the PDS was switched between treated groundwater and desalinated water based on the schedule shown in Table 3-7. Batches of each source waters were prepared weekly following the treatment methods shown in Table 3-1. Source waters were allowed to equilibrate with the pipe materials for at least 3 days before sampling took place, which allowed for multiple flushes of the pipes.

Table 3-7: Iron Flux Experimental Plan

PDS	Re	Source Water
15	50	RO
15	100	RO
15	100	GW
15	150	RO
18	50	RO
18	100	RO
18	150	GW
18	200	RO

3.4.2 Sampling

Analysis from these sampling events was performed on the parameters shown in Table 3-8. Sampling was taken at the influent (I) and effluent (E) ports, with additional sampling for iron at internal sampling ports. The internal sampling was varied for different sampling events.

Table 3-8: Analysis Performed During Iron Flux Experiments

Parameter	**Method of Quantification**
Ammonia	Ammonia Probe
pH	pH Probe
Alkalinity	Titration
UV-254	Spectrophotometer
Dissolved Oxygen	Dissolved Oxygen Probe
Temperature	Dissolved Oxygen Probe
Silica	Spectrophotometer/ICP
Total Chlorine	Spectrophotometer
Turbidity	Spectrophotometer
Apparent Color	Spectrophotometer
Conductivity	Conductivity Probe
Sodium	Spectrophotometer
Chloride	Titration/IC
Sulfate	Spectrophotometer/IC
Total Iron	Spectrophotometer/ICP

3.5 Quality Assurance/Quality Control (QA/QC)

A QA/QC plan was created for this project to ensure the accurate collection and reporting of data. The plan called for duplicate samples to be analyzed on at least 10% of the recorded measurements. 10% of the samples were also spiked with a standard concentration where applicable. Standards from known concentrations were also used to create standard curves. Blank concentrations were also determined from distilled water

to ensure no significant contamination of dilutions and standards occurred. This plan is in agreement with the Standard Methods of the Treatment of Water and Wastewater. Table 3-9 shows the parameters that were measured and the frequency of performed QA/QC procedures.

Table 3-9: QA/QC Procedures Used During Analysis

Parameter	**Blanks (Every Sampling)**	**Standards (Every Sampling)**	**Duplicates (10% of Samples)**	**Spikes (10% of samples)**
Ammonia	X	X	X	X
pH	X	X	X	
Alkalinity	X	X	X	X
Calcium	X	X	X	X
Magnesium	X	X	X	X
UV-254	X		X	
HPC	X		X	
Dissolved Oxygen			X	
Temperature			X	
NPDOC	X	X	X	X
Nitrites	X	X	X	X
Silica	X	X	X	X
Total Chlorine	X	X	X	
Free Chlorine	X	X	X	
Turbidity	X	X	X	
Apparent Color	X	X	X	
Conductivity	X	X	X	
Ortho-Phosphate	X	X	X	X
Total Phosphorous	X	X	X	X
Sodium	X	X	X	X
Chloride	X	X	X	X
Sulfate	X	X	X	X
Copper	X	X	X	X
Zinc	X	X	X	X
Total Lead	X	X	X	X
Dissolved Iron	X	X	X	X
Total Iron	X	X	X	X

4 VERIFICATION OF A NON-LINEAR COLOR RELEASE MODEL

4.1 Abstract

A model for the prediction of color release from a pilot distribution system was created by Imran et al (2005a). The model allows prediction of the release of color from aged cast iron and galvanized steel pipes as a function of water quality and hydraulic residence time. Color was used as a surrogate measurement for iron, which exhibited a strong linear correlation. An anomaly of this model was an absence of a term to account for pH, due to the influent water being well stabilized. A new study performed on the same pilot distribution system was completed to evaluate this model under different pH conditions. The resulting data showed that effluent iron and color values were typically greater in the line with lower pH. The non-linear color model by Imran showed good agreement when the LSI was largely positive, but underpredicted the color release from the lower LSI line. A modification to the Larson Ratio proposed by Imran was able to give a reasonable agreement to the iron data at lower LSI values.

4.1.1 Keywords

Corrosion, Water Distribution, Potable Water, Water Treatment, Water Temperature, Water Quality, Color, Cast Iron

4.2 Introduction

With large amounts of cast iron and galvanized pipes still existing in many water distribution systems, iron release remains a considerable problem. Many different factors contribute to iron release from aged pipes, which makes the problem complicated to solve. High levels of iron can cause many aesthetic problems such as color, turbidity, foul taste and odors. In previous work performed by Imran et al. (2005), a nonlinear model was developed to predict increase in apparent color in a pilot water distribution system (PDS). A wide range of water quality data was collected during this two-year project, which allowed extensive testing and verification. This model showed that chlorides, sulfates, sodium, temperature, dissolved oxygen and hydraulic residence time contributed to an increase in color. The model also showed alkalinity to have a beneficial effect in reducing color, but pH was not a significant term at the 95% confidence level. This finding for pH was explained due to the high LSI of the feed waters. Imran (2005a) also developed a modification to the Larson Ratio, which included sodium, temperature, and HRT terms that showed a better correlation to iron release.

In a new one-year study on the same pilot distribution system, the effects of pH and LSI were examined to verify these models. Two PDS lines were supplied with nearly the same water qualities, one at pH close to pHs and one at pH well above pHs. Changes in iron, color and turbidity were measured in the influent and effluent streams on a regular basis. Periodic changes in source water blends also allowed for the investigation of the effects of other water quality variables on iron release. The resulting data was analyzed

to verify the color release model and Modified Larson Ratio developed by Imran, and to identify the effects of pH on the release of iron.

4.2.1 Research Background

The results of this research were part of a University of Central Florida-Tampa Bay Water-AWWARF tailored collaboration project. The project was designed to evaluate control opportunities for distribution system water quality in a changing water quality environment using inhibitors. This project follows a related project performed from 2002-2004 on the effects of blending on distribution system water quality. Tampa Bay Water (TBW) consists of the subsidiary member governments of Pinellas, Hillsborough and Pasco Counties and the Cities of New Port Richey, St. Petersburg, and Tampa. Contributions have also been made to this project by the American Water Works Association Research Foundation (AWWARF) for this one year study.

4.3 Literature Review

The main goal of a water treatment facility is to provide clean, safe, and tasteful water to all consumers. This can be difficult for utilities to accomplish due to wide networks of piping that vary in pipe material, dimensions, and flow. Deterioration of water quality in distribution systems is so common that most utilities alter their finished water so that it is more resistant to deterioration. Federal standards have been set to maintain a consistent basis of maximum levels of certain water quality parameters known to have adverse health effects. While some corrosion products such as copper and lead have maximum contaminant levels, iron is a secondary standard with a suggested concentration limit of

0.3 mg/L (USEPA 2003). While utilities must focus on compliance with the regulated standards, control of iron release is still important. Consumer complaints frequently deal with the aesthetic qualities like color, turbidity, taste and odor problems, which can be caused by the corrosion of iron pipe. The most frequently listed complaint amongst utilities nationwide is complaints resulting from iron pipe corrosion (McNeil and Edwards 2001). Iron pipe corrosion can also become so severe that pipe blockage or breakage can occur over long periods of time. For these reasons it is in the best interest of a utility to limit iron pipe corrosion and minimize iron release outbreaks with preliminary treatment measures before the finished water is allowed to enter the distribution system.

Studies on iron pipe have been conducted for many decades because the nature of iron pipe corrosion is not consistent. Many factors have been concluded to induce or inhibit iron release under certain conditions. Utilities have often adopted corrosion prevention methods based on the typical water quality they produce everyday. Yet as future regulations on water supplies coupled with increasing consumer demand, more utilities will be forced to look for alternative water sources. Documented problems can arise in distribution systems under changing water qualities, and distribution system water quality can be severely affected.

Many methods have been developed to mitigate iron corrosion. The most common method is to produce finished water that has potential to precipitate calcium carbonate ($CaCO_3$). The precipitation of calcium carbonate inside the pipe will theoretically form a thin coat on the interior pipe surface. This would prevent cathodic/anodic reactions at the

pipe metal surface and prevent the release of iron from the pipe surface. A water with a potential to precipitate $CaCO_3$ is commonly referred to having a positive Langelier Saturation Index (LSI), which means the pH of the water is greater than the pH at which calcium carbonate is saturated in solution (Langelier 1936). LSI is defined below by Snoeyink and Jenkins (1980).

$$LSI = pH - pHs \tag{4-1}$$

Where:

pH is the measured pH of the solution

pHs is the $CaCO_3$ saturation pH of the water, obtained from Equation (2-6)

$$pHs = pK_A - pK_{SO} + pCa - pHCO_3 - \log\gamma_{Ca} - \log\gamma_{HCO3} \tag{4-2}$$

Where:

pK_A is the log of the equilibrium constant for the bicarbonate-carbonate species

pK_{SO} is the solubility product constant for calcium carbonate ($CaCO_3$)

pCa is the log of the molar concentration of calcium in solution

$pHCO_3$ is the log of the molar concentration of bicarbonate in solution

γ is the activity coefficients (for both calcium and bicarbonate)

LSI is a common index used by many utilities and engineers to refer to the corrosivity of the water, where a positive value of LSI is accepted to represent non-corrosive water. It is common practice for utilities to elevate the pH in order to obtain a positive LSI in the finished water. While using LSI is a simplified way of dealing with corrosion problems,

the measures of producing finished water with a positive LSI is not a guaranteed solution for corrosion problems (McNeil and Edwards 2001).

Other corrosion indices have been created based on lab or pilot scale studies. Many of these indices are based on calcium carbonate solubility and share a strong relationship to LSI (Imran 2005b). One corrosion index that is independent of $CaCO_3$ solubility is the Larson Ratio. Larson Ratio incorporates the corrosive effects of chlorides and sulfates against the beneficial properties of alkalinity. The Larson Ratio (LR) is represented by Equation 4- 3, where a ratio greater than 0.5 is considered to be corrosive (Larson & Skold, 1958).

$$LR = \frac{(Cl^{-} + SO_4^{-2})}{(HCO_3^{-})} \tag{4-3}$$

Where:

Cl- is the equivalent concentration of chloride ion [meq/L]

HCO_3^- is the equivalent concentration of bicarbonate [meq/L]

SO_4^{-2} is the equivalent concentration of sulfate [meq/L]

Alkalinity addition has also been shown to help mitigate the problems of iron release. The addition of alkalinity has been reported to help reduce iron release and corrosion rates (McNeil and Edwards 2001), but the addition of alkalinity may have a detrimental effect in increasing copper release. A tradeoff might exist for utilities if alkalinity supplementation is used. Edwards et al. (1996) conducted a study on the feasibility of

commonly accepted corrosion reduction methods. They concluded that increased bicarbonate alkalinity in the finished water increased copper concentrations in a near linear relationship. Thus supplementation of alkalinity can be a double edged sword as a corrosion inhibitor.

pH and alkalinity are related in calcium carbonate solubility, and are generally the two main parameters that are considered to influence iron corrosion. Addition of basic chemicals, such as sodium hydroxide (NaOH), will raise the pH as well as the alkalinity. Separating the effects of pH from alkalinity in corrosion evaluations is difficult. Sarin et al (2004) concluded that increasing the pH from 7.6 to 9.5 reduced the amount of iron released to water in a pilot cast iron distribution system. Low iron levels were reached only after a few months of equilibration at these high pH levels. The study also noted that the influent water supplied to this cast iron pipe was relatively low in alkalinity (<60 mg/L as CaCO3), and that significant increases in alkalinity were found to have an effect in reducing iron release. Alkalinity is also known for increasing buffer intensity, which has also been found to be effective in combating iron corrosion (McNeil 2001).

Temperature has a large effect on most chemical and biological reactions. Thus it is no surprise that it has an effect on corrosion too. pH, solubility, and dissolved oxygen concentrations in water are all directly linked to temperature. Control of temperature of the water in the distribution system is not a feasible option, thus many corrosion control strategies are adapted depending on current seasonal temperatures. Studies by Volk et al. (2000) reported that temperature has a strong relationship with corrosion rates, and that

corrosion control strategies should be changed based on the current season. Their research conducted on annual reactors constructed of cast iron pipe used actual finished water from a utility that practiced corrosion control by dosing zinc orthophosphate corrosion inhibitor.

Dissolved oxygen can be at near saturation levels before entering some distribution systems due to aeration processes. Theoretically, dissolved oxygen is one of the reduced compounds that can fuel the corrosion cell, but studies have mentioned that it can have beneficial effects in reducing iron release in certain instances. Sarin et al. (2003) performed a study on the effects dissolved oxygen has on iron corrosion under stagnant hydrologic conditions. He concluded that dissolved oxygen and other oxidants help to control iron release in aged cast iron pipes. The oxidation of ferrous iron to ferric iron produced harder to release scales that resulted in less iron release.

Dissolved solids are always present in natural waters, and are added to treated water as byproducts of chemical treatment. Common dissolved solids in waters are calcium, sodium, chlorides, sulfates, and bicarbonate. Chlorides and sulfates are commonly referred to as “aggressive” ions because they are believed to be destructive to pipe scale. Calcium and bicarbonate are noted as “passive” ions due to their tendencies to form scale (Butler & Ison 1966; Larson & Skold, 1958).

4.3.1 Review of Iron Release Models

Imran (2005a) developed a color release model based on influent water quality using weekly average data from 14 pilot distribution systems. This model showed that apparent color could be closely predicted based on the following WQ parameters. This model exhibited relatively good correlation ($R^2 = 0.83$) with color data, and was verified using an independent data set. Equation 4-4 shows this model.

$$\Delta C = \frac{(Cl^-)^{0.485} \times (Na^+)^{0.561} \times (SO_4^{-2})^{0.118} \times (DO)^{0.967} \times (T)^{0.813} * (HRT)^{0.836}}{20.7 \times (ALK)^{0.912}} \qquad (4\text{-}4)$$

Where:

ΔC is the change in apparent color: effluent – influent (CPU)

Cl^- is the chloride concentration (mg/L)

Na^+ is the sodium concentration (mg/L)

SO_4^{-2} is the sulfate concentration (mg/L)

DO is the dissolved oxygen concentration (mg/L)

T is the temperature (°C)

HRT is the hydraulic residence time (days)

ALK is the alkalinity (expressed as mg/L $CaCO_3$)

The data also showed that waters low in alkalinity (<80 mg/L as CaCO3) corresponded to significantly higher concentrations of effluent iron. Water quality parameters such as chlorides, sulfates, and dissolved oxygen were statistically significant in elevating effluent color levels based on the model development.

The applicability of this color model to iron values results from the linear relationship found between color and effluent iron concentrations ($R^2 = 0.82$). The linear relationship showed that an increase in color of 1 CPU correlated to an approximate iron concentration increase of 0.013 mg/L. This model does not incorporate pH, conductivity, calcium, silica and UV-254 measurements because they were not determined to be statistically significant using ANOVA at 95% confidence. pH was concluded not be significant because the waters were typically fed into the system with large (> +0.4) LSI values.

Imran et al. (2005b) also evaluated many corrosion indices with data collected from this pilot distribution system. They found that the Larson Ratio had a better correlation to iron and color release than many of the calcium carbonate based indices. They developed the Modified Larson Ratio (MLR) to account for the effects of sodium, temperature and HRT on iron release. These modifications produced a better correlation to the iron data. The equation for the MLR is shown in Equation 4-5.

$$MLR = \frac{(Cl^- + SO_4^{-2} + Na^+)^{1/2} \times (T) \times (HRT)}{(25 \times ALK)} \quad (4\text{-}5)$$

Where:

Cl^- is the concentration of chlorides (mg/L)

SO_4^{2-} is the concentration of sulfate (mg/L)

Na^+ is the concentration of sodium (mg/L)

T is the temperature (^oC)

HRT is the hydraulic retention time (days)

ALK is the alkalinity of the sample (mg/L $CaCO_3$)

4.4 Methods and Materials

The pilot distribution system used for this analysis is the same used for the originally developed models. This site is located at the Cypress Creek Treatment Facility in Land O' Lakes, FL. The PDS construction remained unchanged but several operational changes were made to evaluate corrosion inhibitors. The PDS data used for this analysis comes from two PDS lines (PDS 13 and PDS 14) that contained no corrosion inhibitor.

4.4.1 Site Description

Fourteen pilot distribution systems were constructed from segments of cast iron (CI), lined cast iron (LCI), polyvinyl chloride (PVC) and galvanized steel (G) sections. The effluent water from the PDS were fed to loops of copper tubing containing lead coupons to simulate lead soldered home plumbing systems. The PDS design was intended to simulate actual distribution systems used by the TBW utilities. All pipe materials used in construction came from actual pipelines serving the Tampa Bay area. The approximate lengths of each section were 20 feet of PVC, 20 feet of LCI, 12 feet of CI, and 40 feet of G. PDS 1-12 were used to evaluate different doses of four corrosion inhibitors, while PDS 13 and PDS 14 contained only the influent water with no inhibitor. The hydraulic retention time was kept constant at two days for all PDS.

4.4.2 PDS Operation

Influent water to the PDS was made of a blend of treated groundwater, surface water, and desalinated water. Batches of each source waters were prepared weekly following the treatment methods shown in Table 4-1. Four different blends were used to encapsulate expected future TBW water quality. The composition of the blend was kept constant for three month periods described in Table 4-2. Flushing of the PDS systems was conducted on a biweekly basis with 5 pipe volumes, while the copper tubing was flushed on a daily basis. After each three month phase, the pipelines were burned with free chlorine for 1 week.

4.4.3 Modifications to Plant Operation

The overall goal of the Tampa Bay Water II project was to evaluate the effects of corrosion inhibitors under changing water qualities. Four corrosion inhibitors (blended ortho-phosphate, ortho-phosphate, zinc ortho-phosphate and silicate) were added to the influent blend in each phase of the 1-year project to evaluate the effects on metal release. Three target doses for each inhibitor were added to a separate PDS to evaluate inhibitor dosing. PDS lines 13 and 14 were supplied with control blend with no added inhibitor. PDS 13 was supplied with the water near pHs, and PDS 14 was supplied with water at a target pH well above pHs. The water for PDS 13 was made by adding of a small amount of hydrochloric acid to a separate tank containing blend water. This addition resulted in slight differences in influent water quality between PDS 13 and PDS 14. The most notable water quality differences resulted in increased chlorides and decreased alkalinity resulting from the acid reacting with the blend water. These control lines allowed for

comparisons of traditional LSI corrosion control methods to dosing corrosion inhibitors, but were also amendable to use for comparisons to previous TBW findings. The data used for this analysis incorporates only data from PDS 13 and 14, and comprises a much smaller data set than was used for the original model development.

4.4.4 Sampling

Sampling from the PDS lines followed a schedule according to Table 4-3. Sampling was taken at the influent (I) and effluent (E) ports on a weekly basis. These samples were always taken at least 48 hours after the new blend was made to ensure the previous week's blend was entirely flushed out. A wide variety of water quality parameters were analyzed under this sampling plan to allow for many simultaneous studies. Analysis followed a quality assurance-quality control (QA/QC) plan described in Table 4-4.

4.4.5 LSI Calculation

LSI was used as a measure of how much acid was added to the PDS 13 influent water. PDS 14 was typically fed with water with LSI values of targeted to be greater than +0.4. PDS 13 was fed with the same blend that was adjusted to target an LSI of 0. Over the 48 hour period between making the blend and sampling, changes in pH occurred due equilibrium reactions with the atmosphere that resulted in some deviation in LSI values from their initial targets. LSI was determined by using a modification of Equation 4-1, using temperature and conductivity corrections.

$$LSI = pH - pHs \tag{4-6}$$

Where pH_S was determined by Equation 4-7:

$$pHs = K - log_{10}\left(\frac{Ca}{100{,}000}\right) - log_{10}\left(\frac{Alk}{50{,}000}\right) + 5A\left(\frac{\sqrt{I}}{I+\sqrt{I}} - 0.3I\right) \quad (4\text{-}7)$$

Where:

K and *A* are temperature dependent constants found in Table 4-5

Ca is the calcium concentration as $CaCO_3$

Alk is the alkalinity concentration as $CaCO_3$

I is the ionic strength

The ionic strength may be approximated by Equation 4-8:

$$I = 1.6 \times 10^{-5} \times (COND) \quad (4\text{-}8)$$

Where:

COND is the conductivity in micro Siemens/cm (μS/cm).

4.5 Results

4.5.1 Data Analysis

From the onset of data collection, PDS 13 experienced much greater water quality deterioration than PDS 14. From the average values listed in Table 4-6, iron release in PDS 13 nearly doubled PDS 14, which corresponded with higher color and turbidity values as well. Closer investigation of the distribution of iron release for both PDS revealed that they were indeed different. A box plot shown in Figure 4-1 shows the spread of iron concentrations for PDS 13 and PDS 14. The box represents the 25th to 75th

percentile data, with the middle line denoting the median value. The upper and lower lines represent the 10^{th} and 90^{th} percentile limits. The dots represent individual data points outside the 10-90^{th} percentile. The plots clearly show that iron concentrations in PDS 13 were significantly greater than PDS 14 at all percentiles, especially at the maximum iron release (0.47 mg/L in PDS 13 versus 0.18 mg/L in PDS 14). Harsh conditions occurred during the study, including temperatures greater than 25^{o}C and chloride and sulfate concentrations as large as 70 and 100 mg/L, respectively. Even under these aggressive conditions, PDS 14 never violated the secondary iron standard of 0.3 mg/L during the entire study, while PDS 13 violated several times. Using this data it is concluded that well stabilized waters with sufficient alkalinity (>100 mg/L $CaCO_3$) were effective measures to control iron release in the PDS. These results were expected as they follow commonly accepted theories involving LSI and the inhibitory properties of alkalinity on iron release.

4.5.2 Model Testing

The data collected from PDS 13 and PDS 14 was used to assess the color release model described previously in Equation 4-4. The results showed that model predicted the color in PDS 14 with reasonable accuracy. The average difference in the predicted color values and the actual color data was less than 1 CPU, with no strong trend of over or under predictions. Figure 4-2 presents a summary of predicted versus actual color values for PDS 14.

The response in PDS 13 was quite different, as the model under-predicted over two-thirds of the data points. The model only predicted slightly higher color release for PDS 13 than PDS 14, but actual color data was substantially higher. The model averaged an under-prediction of nearly 4 CPU, and severely under-predicted the larger color values. Figure 4-3 shows the actual color data from PDS 13 plotted with the predicted color values. From these results it was evident that the color release model was applicable only under the well stabilized conditions from which it was derived (LSI > 0.4).

4.5.3 Modified Larson Ratio Testing

The PDS 13 data was also used to evaluate the MLR shown in Equation 4-5. The MLR for PDS 13 correlated fairly well with iron and color data and exhibited a good visual trend, despite some scatter. Even though the MLR equation has no direct term to account for pH, the model was able to predict increases in PDS 13 iron concentrations based on increased chlorides and decreased alkalinity. Larger values of iron were recorded during summer months, in which the higher temperatures resulted in a significant increase in MLR values. The relationship between MLR and delta iron concentrations is shown in Figure 4-4.

4.5.4 LSI Relationship to Data

Preliminary explanations for the differences in PDS 13 and PDS 14 iron and color data relate to the differences in LSI values. While PDS 13 had an average LSI value that was much less than the average LSI value in PDS 14, iron and color relationships with LSI were inconclusive. A slight trend of decreasing iron with increasing LSI can be seen in Figure 4-5, but the data shows occasional high iron release occurred despite high influent

LSI values. These high iron values occurred during unfavorable finished water conditions (high chlorides, high sulfates, high temperature), in spite of a high LSI. Based on these results it is concluded that use of the LSI should be limited and would not be adequate as a definitive predictor of iron release. Unfavorable water quality such as high sulfates, chlorides, and temperature also demonstrated a tendency to aggravate iron scales. Imran's (2005b) correlation of the LSI with iron measurements from TBWI developed a similar general trend, but had a modest overall correlation ($R^2 = 0.3$).

4.5.5 Modeling of PDS 13

Attempts to formulate a new comprehensive non-linear power model predicting iron release were also analyzed. The goal of this effort was to develop a new model that included a term related to calcium carbonate equilibrium (pH, LSI, etc.) with the reduced pH values used in this study. The new non-linear model was developed in the same manner as the original model, using an analysis of variance (ANOVA) to eliminate non-significant variables at the 95% confidence level. The data collected for this analysis pales in comparison to the data collected for original model development in the range of most water quality variables. Correspondingly, the results of this analysis would not be a complete analysis, due to the limitations of the experimental plan. The results of the new ANOVA testing revealed that pH, pHs, and LSI were not significant variables during separate trials. The resulting model is shown in Equation 4-9, and Figure 4-6 shows the relationship between the predicted values with the actual data.

$$\Delta Fe = 0.0572 \times (Cl^-)^{1.62} \times (ALK)^{-1.18} \times (0.832)^{\frac{TEMP}{10}} \quad (4\text{-}9)$$

Some parameters were eliminated due to confounding relationships between variables. These removed variables include dissolved oxygen (highly correlated with temperature), sodium (highly correlated with chlorides), and sulfates (highly correlated with alkalinity). Variables with high inter-correlation lead to the elimination of one variable by the dominance of the other variable in the model equation. When surface water comprised a large amount of the blend water, sulfate concentrations rose significantly with a corresponding drop in alkalinity from less groundwater. The final parameters that were found to be significant in the new model were all parameters that are incorporated in the MLR. The author recommends the use of the MLR despite the slight improvement in fit with the newly developed non-linear model. The MLR was developed using a much larger and more complete database than the data used to create the new non-linear model, thus the applicability of the MLR is much greater.

4.6 Conclusions and Recommendations

The results of the study of PDS 13 and PDS 14 revealed the average iron concentration was significantly greater in PDS 13, with a much greater tendency to exceed the secondary standard. Consequently, the non-linear color release developed by Imran was valid in predicting color release in PDS 14, but not in PDS 13. The corresponding increase in color and iron from PDS 13 were fairly well described by the Modified Larson Ratio, but not by LSI.

A slight trend of decreasing iron with increasing LSI was observed, but relatively high iron values still occurred at high influent LSI values. Based on this research it was seen

that water quality parameters other than the LSI had better correlations with iron release. Therefore it is cautioned that LSI is not suitable as a universal predictor of iron release.

An attempt to model the data with a non-linear power model resulted in only slightly better correlations to iron data than the MLR. The pH, LSI, and pHs were all not demonstrated to be significant variables for this data set in separate model trials at 95% confidence level.

The resulting analysis from PDS 13 and PDS 14 showed that Imran's color release model is recommended under similar well-stabilized conditions that were used for model development. The MLR is recommended as a better predictor of iron release under more aggressive conditions.

Due to the limitations of this study, a full study of the effects of pH and LSI on iron release were unable to be performed. Alternate methods of raising and lowering pH, such as lime addition and recarbonation, would need to be investigated to fully separate the effects of water quality from pH and LSI. It is also emphasized that the effects of water quality variation was only evaluated under a small range of pH and that hydraulic effects were not examined.

4.6.1 Further Study

A more complete review of the work performed in this chapter is presented in Appendix A. The appendix contains minimum and maximum water quality values for the current

study as well as the minimum, maximum, and average data used for the original color model development.

4.7 Acknowledgment

The authors wish to acknowledge Chris Owen, Tampa Bay Water Authority Quality Assurance Officer, who was the TBW Project Coordinator, and Roy Martinez, AWWA Research Foundation Senior Account Officer, who was the AWWARF Project Officer, and the following Member Governments: Pinellas County, Hillsborough County, Pasco County, Tampa, St. Petersburg, and New Port Richey. Pick Talley, Robert Powell, Dennis Marshall and Oz Wiesner from Pinellas County, and Dr. Luke Mulford from Hillsborough County are also specifically recognized for their contributions. Several UCF Environmental Engineering students and faculty also contributed significantly to this project and are recognized for their efforts.

4.8 Tables and Figures

Table 4-1: Source Water Types

Water Type	Treatment
Ground Water (GW)	Treatment by aeration, free chlorine, added ammonia to form combined chlorine.
Surface Water (SW)	Treatment by ferric sulfate coagulation, flocculation, settling, filtration, disinfection by ozonation, biologically activated carbon filtration, disinfection residual from combined chlorine.
Desalinated Water (RO)	Treatment by reverse osmosis membranes, aeration, disinfection by free chlorine, added ammonia to form combined chlorine, dissolved salt addition to simulate desalination process.

Table 4-2: Source Water Composition by Phase

Phase	% GW in Blend	% SW in Blend	% RO in Blend
I (Feb – May 2006)	62	27	11
II (May - Aug 2006)	27	62	11
III (Aug – Nov 2006)	62	27	11
IV (Nov 2006 - Feb 2007)	40	40	20

Table 4-3: PDS 13 and 14 Sampling Frequency

Parameter	Sampling Frequency	Sample Points*	Method of Quantification
Ammonia	Weekly	I,E	Ammonia Probe
pH	Weekly	I,E	pH Probe
Alkalinity	Weekly	I,E	Titration
Calcium	Weekly	I,E	Titration/ICP
Magnesium	Weekly	I,E	Titration/ICP
UV-254	Weekly	I,E	Spectrophotometer
HPC	Weekly	I,E	Plate Count
Dissolved Oxygen	Weekly	I,E	Dissolved Oxygen Meter
Temperature	Weekly	I,E	Dissolved Oxygen Meter
NPDOC	Weekly	I,E	TOC Analyzer
Nitrites	Weekly	E	Spectrophotometer
Silica	Weekly	I,E	Spectrophotometer/ICP
Total Chlorine	Weekly	I,E	Spectrophotometer
Free Chlorine	Weekly	I,E	Spectrophotometer
Turbidity	Weekly	I,E	Spectrophotometer
Apparent Color	Weekly	I,E	Spectrophotometer
Conductivity	Weekly	I,E	Conductivity Probe
Ortho-Phosphate	Twice Weekly	I,E	Spectrophotometer
Total Phosphorous	Weekly	I,E	ICP
Sodium	Weekly	I,E	Spectrophotometer
Chloride	Weekly	I,E	Titration/IC
Sulfate	Weekly	I,E	Spectrophotometer/IC
Copper	Weekly	I,E	ICP
Zinc	Weekly	I,E	ICP
Total Lead	Weekly	I,E	ICP
Dissolved Iron	Weekly	I,E	ICP
Total Iron	Weekly	I,E	Spectrophotometer/ICP

* I and E denotes Influent and Effluent Sample Ports

Table 4-4: Quality Assurance and Quality Control Schedule

Parameter	**Blanks (Every Sampling)**	**Standards (Every Sampling)**	**Duplicates (10% of Samples)**	**Spikes (10% of samples)**
Ammonia	X	X	X	X
pH	X	X	X	
Alkalinity	X	X	X	X
Calcium	X	X	X	X
Magnesium	X	X	X	X
UV-254	X		X	
HPC	X		X	
Dissolved Oxygen			X	
Temperature				
NPDOC	X	X	X	X
Nitrites	X	X	X	X
Silica	X	X	X	X
Total Chlorine	X	X	X	
Free Chlorine	X	X	X	
Turbidity	X	X	X	
Apparent Color	X	X	X	
Conductivity	X	X	X	
Ortho-Phosphate	X	X	X	X
Total Phosphorous	X	X	X	X
Sodium	X	X	X	X
Chloride	X	X	X	X
Sulfate	X	X	X	X
Copper	X	X	X	X
Zinc	X	X	X	X
Total Lead	X	X	X	X
Dissolved Iron	X	X	X	X
Total Iron	X	X	X	X

Table 4-5: Temperature Dependent Constants for LSI Calculations

Temperature (^{o}C)	K	A
5	2.16	0.494
10	2.08	0.498
15	2.00	0.502
20	1.93	0.506
25	1.85	0.511
30	1.78	0.515

Table 4-6: Average Water Quality for PDS 13 and PDS 14

Parameter	PDS 13	PDS 14
Delta Iron (mg/L)	0.147	0.083
Delta Turbidity (NTU)	0.768	0.291
Delta Color (CPU)	14	7
Predicted Color (CPU)	10	8
pH (Units)	7.74	7.97
LSI (Units)	0.28	0.56
Sodium (mg/L)	32	28
Chlorides (mg/L)	75	57
Sulfates (mg/L)	74	75
Alkalinity (mg/L as $CaCO_3$)	130	139
Dissolved Oxygen (mg/L)	8.34	8.27
Temperature (^{o}C)	23.2	23.5
Calcium (mg/L)	70	72
Magnesium (mg/L)	7	7
Total Chlorine (mg/L as Cl_2)	4.6	5.1
Silica (mg/L as SiO_2)	8.4	8.5
Modified Larson Ratio (Units)	0.21	0.18

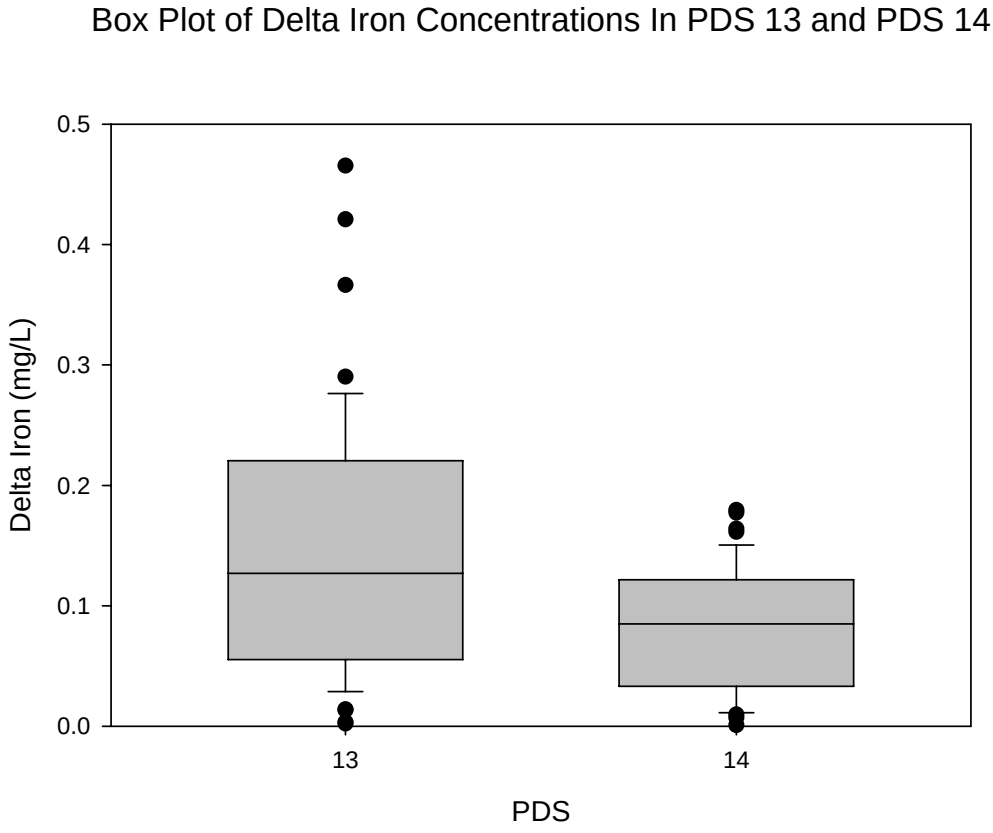


Figure 4-1: Box Plots of Iron Data

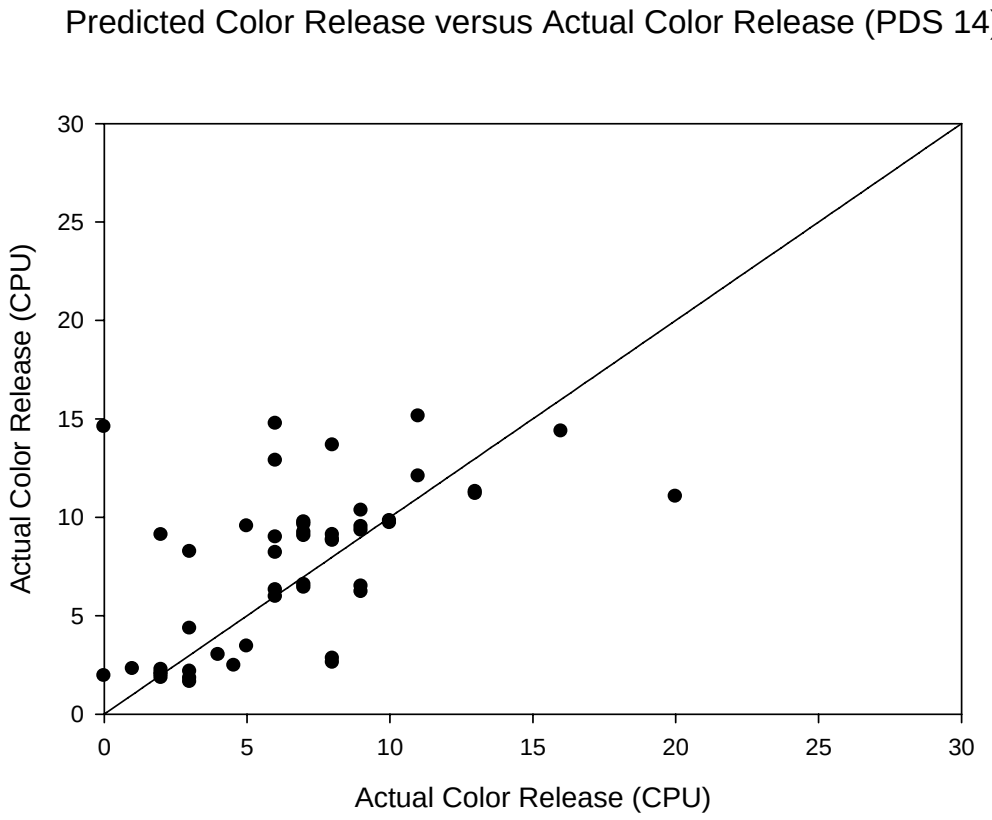


Figure 4-2: PDS 14 Predicted Versus Actual Color

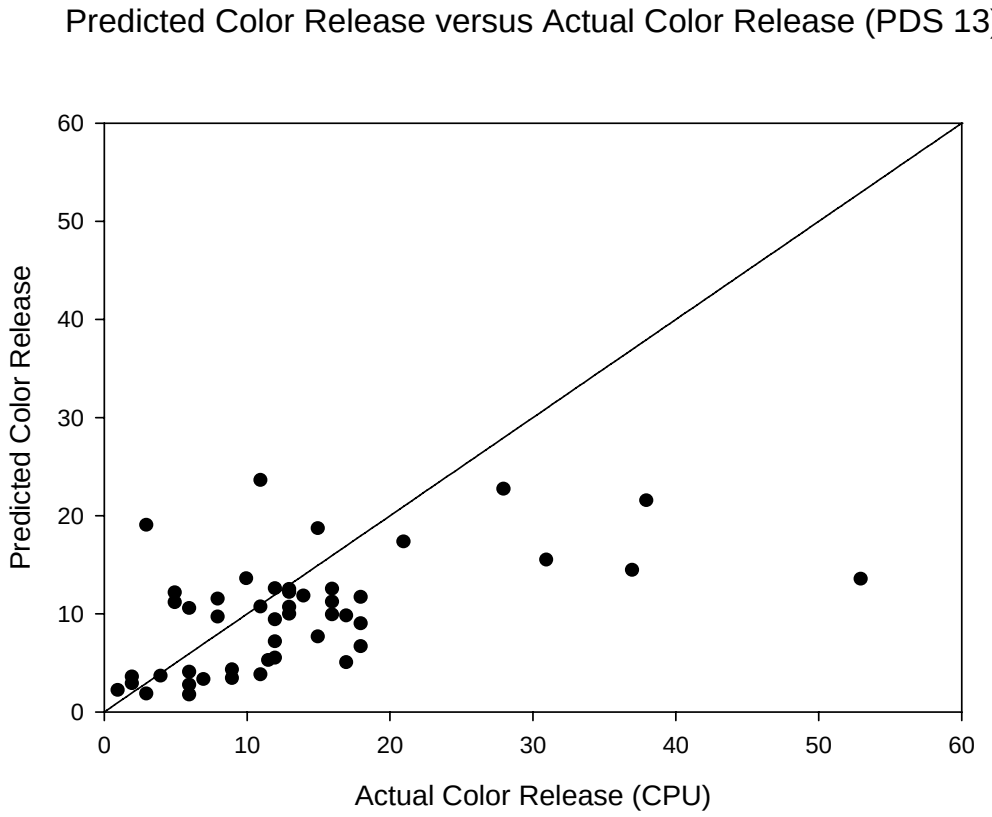


Figure 4-3: PDS 13 Predicted Versus Actual Color

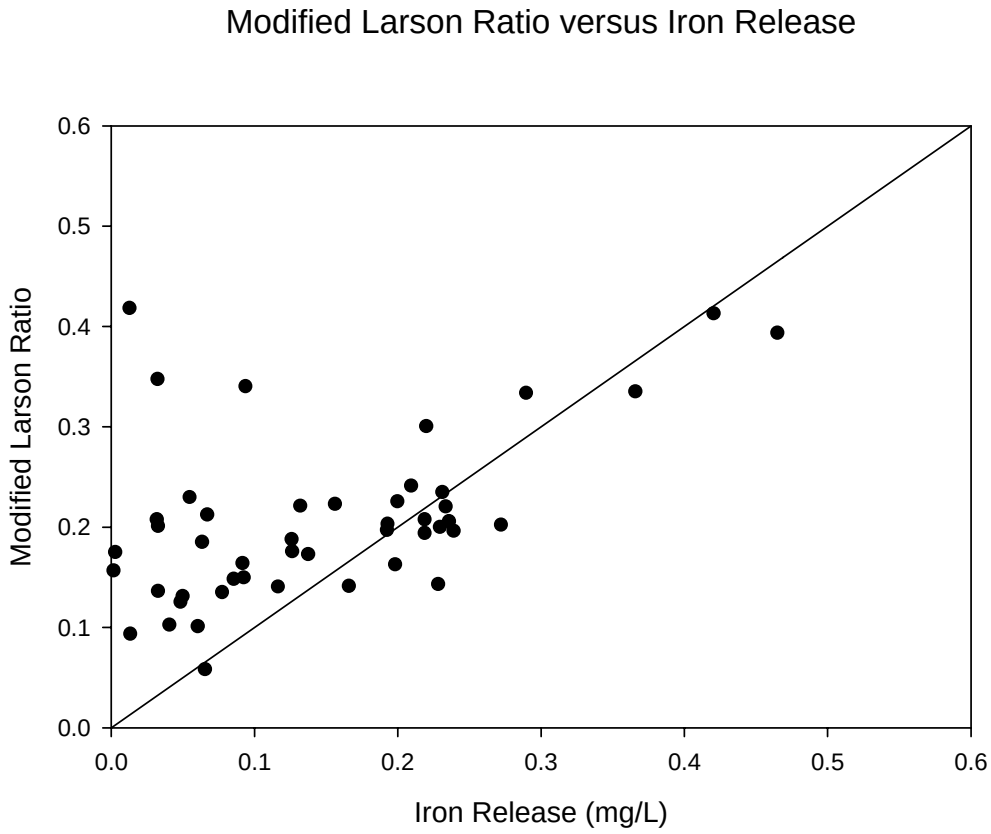


Figure 4-4: MLR Versus PDS 13 Iron Data

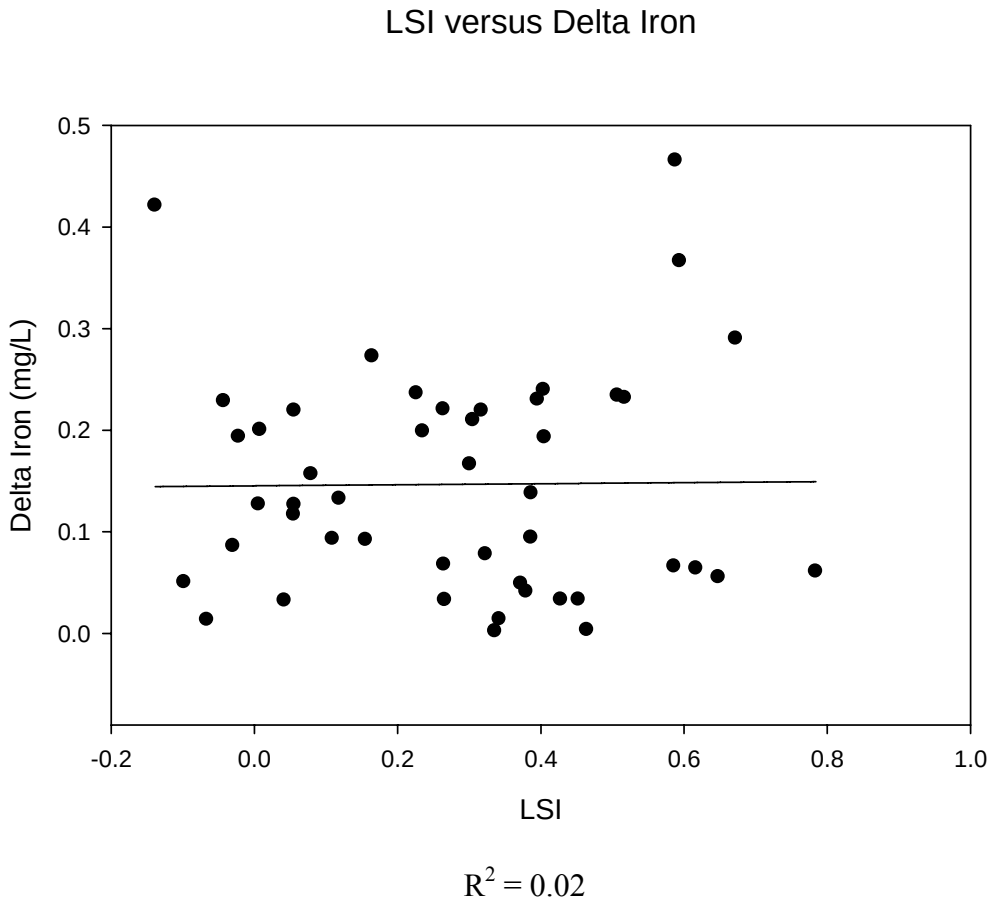


Figure 4-5: LSI Correlation with Iron Release

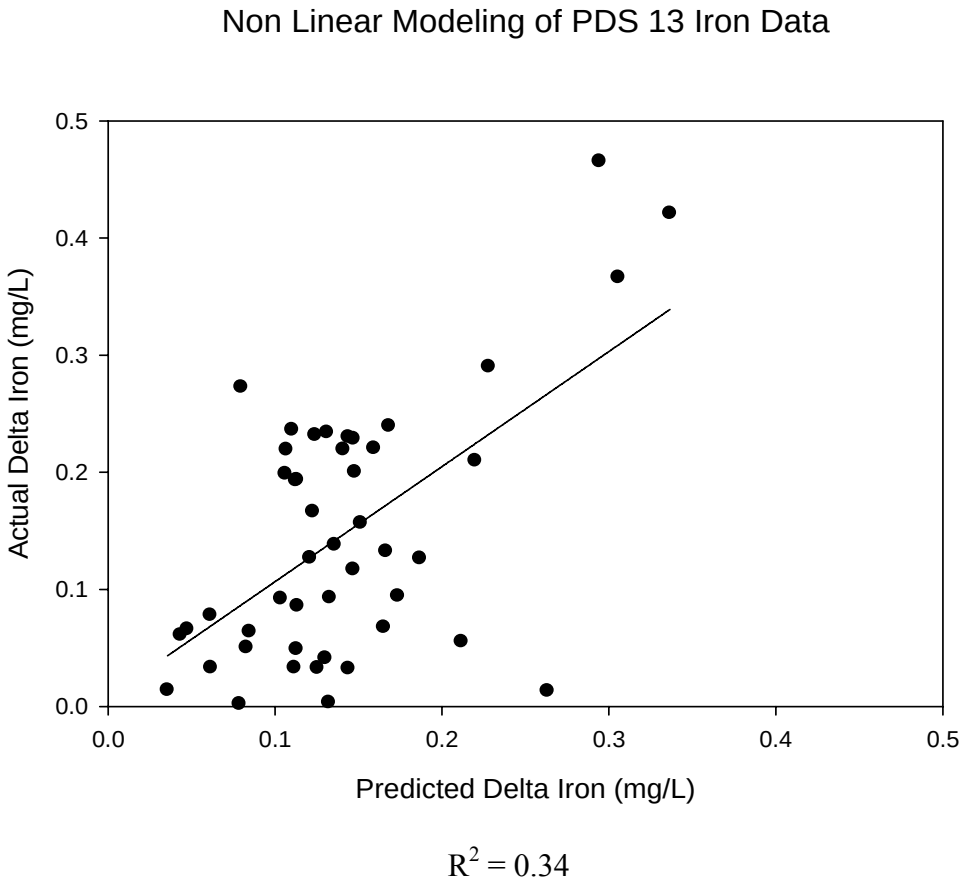


Figure 4-6: Predicted Versus Actual Iron Release for New Model

4.9 References

1. Benefield L.; Judkins, J.; & Weand, B., 1980. *Process Chemistry for Water and Wastewater Treatment*, Prentice Hall, New Jersey.
2. Butler, G. & Ison, H., 1966. *Corrosion and its Prevention in Waters*. Reinhold Publishing, New York.
3. Edwards, M.; Schock, M.; & Meyer, T., 1996. Alkalinity, pH and Copper Corrosion By-product Release. *Jour. AWWA,* 88:3:81.
4. Imran, S. et al, 2005a. Red Water Release in Drinking Water Distribution Systems. *Jour. AWWA*, 97:9:93.
5. Imran, S. et al, 2005b. Modified Larsons Ratio Incorporating Temperature, Water Age, and Electroneutrality Effects on Red Water Release. *Jour. ASCE*, 131:11:1514.
6. Langelier, W., 1936. The Analytical Control of Anti-Corrosion Water Treatment *Jour. AWWA,* 28:10:1500.
7. Larson, T. & Skold, R., 1958. Laboratory Studies Relating Mineral Water Quality of Water to Corrosion of Steel and Cast Iron. *Corrosion,* 14:6:43.
8. McNeill, L. & Edwards, M., 2001. Iron Pipe Corrosion in Distribution Systems. *Jour. AWWA*, 91:7:93.
9. Sarin P.; Snoeyink, V.; Lytle, D. & Kriven, W., 2003. Iron Release from Corroded, Unlined Cast Iron Pipe. *Jour. AWWA*, 95:11:85.

10. Sarin, P.; Snoeyink, V.; Lytle, D.; & Kriven, W., 2004. Iron Corrosion Scales: Model for Scale Growth, Iron Release, and Colored Water Formation. *Jour. Env. Eng.*, 130:4:364.
11. USEPA, 2003. *National Primary Drinking Water Standards*, Washington, D.C.
12. Volk, C.; Dundore, E.; Schiermann, J.; & LeChevallier M., 2000 Practical Evaluation of Iron Corrosion Control in a Drinking Water Distribution System. *Wat. Res.*, 34:6:1967.

5 VERIFICATION OF A NOVEL IRON FLUX MODEL

5.1 Abstract

An iron flux model was developed on a pilot distribution system by Mutoti et al. (2007a). The model proposes that the iron flux under laminar flow conditions is constant, while the iron flux is linearly related to the Reynolds Number under turbulent conditions. The constants for the model were empirically derived from experiments at different hydraulic conditions with a constant water quality. This model incorporates the color release models developed by Imran et al. (2005) to calculate flux values from different water qualities. A limited number of experiments were performed in the current study using desalinated and ground water sources at Reynolds Numbers less than 250. The results showed that the iron flux for cast iron pipe was approximately one-half of the predicted values from Mutoti. This discrepancy may be caused by more extensive flushing of the pipes performed on the current experiments which allowed attainment of a true steady state. Model changes were proposed to distinguish between near stagnant flow and the upper laminar region, with the upper laminar region showing a slight linear increase. Predictions using the galvanized flux model were not accurate due to an inferior color release model that was developed for galvanized pipes. The model exhibits a high dependence on sulfate concentrations, but concentrations of sulfates in the current experiments were low. This led to low predicted flux values when the actual data showed

otherwise. A new galvanized model was developed that contained original data and data gathered from the current experiments. The results using the new model showed great improvement over the old model, but the new model was developed from a limited data set and was not able to be independently tested.

5.1.1 Keywords

Verification, Mathematical Models, Water Pipelines, Pipes, Data Analysis

5.2 Introduction

Research by Mutoti et al. (2007a) developed an iron release model from cast iron and galvanized pipes based on steady state release of iron films. Their research showed that the majority of the iron release in a pilot distribution system comprised of aged water pipes was in the particulate form. This supports the notion that the majority of the iron release from aged pipes is a result of the breakdown of existing iron scales rather than from actual direct corrosion of the pipe surface. From this observation, a model was derived that was based on a mass balance of iron as it traveled through the pipe. The increase in iron was modeled as a zero-order reaction based solely on pipe geometry, water quality and flow conditions. The iron flux was approximately constant under laminar conditions (Reynolds Numbers < 2000) and the iron flux was proportional to the Reynolds Number under turbulent conditions. Verification of this model was also reported with independent data (Mutoti 2007b).

The objectives of this research are to elaborate on the iron flux under low flow regimes where iron, color and turbidity problems have been reported to be more severe. Experiments were designed to measure iron concentrations at sections along reaches of cast iron and galvanized pipe. The experiment incorporated two different water qualities to evaluate passive (groundwater) and aggressive (desalinated water) conditions.

5.2.1 Research Background

The results of this research were part of a University of Central Florida-Tampa Bay Water tailored collaboration project. The project was designed to evaluate control opportunities for distribution system water quality in a changing water quality environment using inhibitors. This project follows a related project performed from 2002-2004 on the effects of blending on distribution system water quality (TBWI). Tampa Bay Water (TBW) consists of the subsidiary member governments of Pinellas, Hillsborough and Pasco Counties and the Cities of New Port Richey, St. Petersburg, and Tampa. Contributions have also been made to this project by the American Water Works Association Research Foundation (AWWARF) for this multi-year study.

5.3 Literature Review

Even if the finished water produced from a plant might meet all federal requirements, the quality of the water may deteriorate in the distribution system. Depending on piping material, undesired additives such as metals, particulates, and microorganisms may be released into the water under certain circumstances. These products result from the interactions of water with iron, copper, and lead pipes that allow corrosion to take place.

While copper and lead are regulated contaminants that are known to cause long-term health effects, iron is not known to have any significant detrimental health effects and is an essential nutrient to the human body. Iron is listed as a secondary standard, with a suggested concentration limit of 0.3 mg/L, due the metallic taste and reddish color it imparts to water (USEPA 2003). Controlling iron release is still a priority, because of the damaging effects it can have in staining clothes and bathroom fixtures. Other problems can arise from the formation of large iron tubercules on the inside pipe walls. These tubercules can grow quite large and severely reduce the flow capacity of the pipe (Curry 1978). A survey of the 100 largest AWWARF participating utilities found that the most frequently listed complaints stem from the corrosion of cast iron pipes (McNeil and Edwards, 2001). The maintenance of distribution systems is also an expensive undertaking. The EPA estimates that for a typical utility, distribution system comprises the majority of capital costs, and that the replacement cost of distribution systems nationwide is well into the billions of dollars (Mullen and Ritter 1980). For these reasons it is in the best interest of a utility to contain iron release outbreaks with preliminary treatment measures before the finished water is allowed to enter the distribution system.

Iron release from cast iron and galvanized pipes occurs because of corrosion. Corrosion is a process in which a metal is oxidized by the environment around it. Corrosion can occur by several mechanisms resulting from extreme temperatures, acidified environments, corrosive soils, connections of dissimilar pipe materials, and physical stresses (Holler 1974). Other corrosion is directly due to the water quality and flow conditions inside the pipe. Internal iron pipe corrosion can occur because the finished

water has an oxidizing potential due to presence of dissolved oxygen in the water. Finished waters generally have substantial dissolved oxygen due to aeration processes and natural equilibrium with the atmosphere. The theorized corrosion reactions of iron are shown as Equations 5-1 through 5-4, which were developed by Butler and Ison (1966) as an electrochemical cell with a reaction at the anode and a reaction at the cathode. The formed iron and hydroxide ions can then react to form a precipitate that can be released into the water.

$$2Fe \rightarrow 2Fe^{+2} + 4e^{-} \quad (5\text{-}1)$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \quad (5\text{-}2)$$

$$2Fe^{+2} + 4OH^{-} \rightarrow 2Fe(OH)_2 \quad (5\text{-}3)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad (5\text{-}4)$$

These reactions represent the corrosion process on a molecular scale. Over time, these reactions can be replicated, creating an iron scale that would coat the interior of the pipe. This scale can become dislodged and release into the bulk stream from changes in flow patterns or changes in water quality.

Corrosion of galvanized pipes occurs differently than cast iron pipes due to the zinc plating on the surface of the pipe. This surface is meant to inhibit corrosion rates and protect the iron underneath. Kirmeyer (1983) reported that galvanized pipes corrode in two stages. First the zinc coating is removed and then the bare iron corrodes releasing

iron products. In well-aged galvanized pipes, the galvanized coating has usually been stripped away and the pipe acts similar to a cast iron pipe.

Iron release has also been related to stagnant water conditions (McNeil and Edwards, 2001). At low or no flow regions in the distribution system, iron scales have increased contact time with the water which allows for more release. Iron release has also been reported to increase with flow rates in the turbulent regions by physical shearing of the scale (Pisigan and Singley, 1987)

Research studies have been designed to identify the important parameters to corrosion. Relationships between iron corrosion and common water quality variables have been identified, none as popular as the Langelier Saturation Index (LSI). LSI is a common index used by engineers to refer to the corrosivity of the water, where a positive value of LSI is accepted to represent non-corrosive water. It is based on water conditions that involve the precipitation of calcium carbonate (Langelier 1936). It is common for utilities to elevate the pH in the finished water to obtain a positive LSI. While LSI is a simplified way of dealing with corrosion problems, the measures of producing finished water with a positive LSI may or may not contribute to solving corrosion problems (McNeil and Edwards, 2001). Producing finished water with a high potential to precipitate $CaCO_3$ may also create excessive scale and reduce carrying capacity. Costello (1984) recommended that efforts to reduce scale formation should occur after the initial protective scale coating has formed in the system.

Other common corrosion indices such as the Aggressiveness Index and the Ryznar Index are based on calcium carbonate solubility and bear strong relationships to LSI (Imran et al. 2005a, Rossum and Merrill 1980). Other indices like the Larson Ratio incorporate the effects of other water quality parameters thought to promote or disrupt iron scales (Larson and Skold 1958). The ratio incorporates the aggressive effects chlorides and sulfates have against iron scales to the beneficial scale building effects of bicarbonate. High temperatures have also been implicated to increase corrosion rates (Volk et al., 2000).

Alkalinity supplementation has also been documented to help reduce iron release and corrosion rates (McNeil and Edwards, 2001). Drawbacks to alkalinity supplementation arise from studies relating alkalinity to increasing copper release. Edwards et al. (1996) study on the feasibility of commonly accepted corrosion reduction methods concluded that increased amounts of bicarbonate alkalinity in the finished water increased copper concentrations in a near linear relationship. Direct alkalinity addition with sodium bicarbonate also inherently raises conductivity and TDS levels that can have a negative effect on iron release (Shull 1980). Thus supplementation of alkalinity can be a double edged sword as a corrosion inhibitor.

5.3.1 Review of Work Performed in TBW I

The initial TBWI project examined relationships between water quality and iron (color) release in cast iron and galvanized pipes. The data showed that finished waters containing less than 80 mg/L as $CaCO_3$ of alkalinity corresponded to significantly higher

concentrations of effluent iron. Other water quality parameters such as chlorides, sulfates, sodium and dissolved oxygen were also shown to be significant in elevating effluent color (and iron) levels (AWWARF, 2006).

An iron release model and an iron flux model were developed using TBWI data by Imran et al. (2005) and Mutoti et al. (2007) respectively. The model developed by Imran predicted the color release from the pilot distribution system. In TBW I, 14 hybrid pipelines were constructed from similar sections of 4 common piping materials (unlined cast iron, lined cast iron, polyvinyl chloride, and galvanized steel). These lines were fed with different blends of treated source waters, which provided a comprehensive database for model development. The pilot distribution system also incorporated four lines constructed of a single material to evaluate the effects of pipe material on effluent water quality. Experiments by Mutoti on cast iron and galvanized pipe investigated the effects of iron release under different flow conditions. Zero-order models were developed which related iron release to pipe geometry and hydraulic residence time. Water quality was kept constant during these experiments, but adjustments for water quality were provided through the incorporation of the Imran color release model.

The Imran et al. (2005) color release model is displayed as Equation 5-5. The parameters incorporated into this model were determined to be significant by an analysis of variance (ANOVA) at the 95% confidence level. This model closely predicted ($R^2 = 0.83$) actual color values recorded in the field.

$$\Delta C = \frac{(Cl^-)^{0.485} \times (Na^+)^{0.561} \times (SO_4^{-2})^{0.118} \times (DO)^{0.967} \times (T)^{0.813} * (HRT)^{0.836}}{20.7 \times (ALK)^{0.912}} \quad (5\text{-}5)$$

Where:

ΔC is the change in apparent color: effluent – influent (CPU)

Cl^- is the chloride concentration (mg/L)

Na^+ is the sodium concentration (mg/L)

SO_4^{-2} is the sulfate concentration (mg/L)

DO is the dissolved oxygen concentration (mg/L)

T is the temperature (°C)

HRT is the hydraulic residence time (days)

ALK is the alkalinity (expressed as mg/L $CaCO_3$)

A model predicting the color release from galvanized pipe was also created from data gathered on the galvanized pipeline. The model shown as Equation 5-6 incorporated a smaller data set and differs slightly from the hybrid model.

$$\Delta C = 10.71 \times (ALK)^{-1.62} \times (Si)^{-0.55} \times (SO_4^{-2})^{1.12} \times (T)^{1.06} \quad (5\text{-}6)$$

Where:

ALK is the alkalinity (expressed as mg/L $CaCO_3$)

SO_4^{-2} is the sulfate concentration (mg/L)

Si is the silicate concentration (expressed as mg/L SiO_2)

T is the temperature (°C)

Color release was related to iron release through a strong linear relationship ($R^2 = 0.82$). Equation 5-7 demonstrates the use of color as a surrogate parameter for iron, which is more amenable to field testing.

$$\Delta Fe = 0.0132 \times (\Delta C) \tag{5-7}$$

Where:

ΔFe is change in iron concentration from influent to effluent in mg/L

The derivation of the Mutoti et al. flux model results from a steady state mass balance of iron inside the pipe. Their study showed most of the iron release from aged pipes was in the particulate form. This implied that the iron release is influenced more by the removal of iron scales than from direct corrosion of the pipe material. With this assumption, the iron release was modeled as a mass of iron removed from the interior pipe surface area over time. Equation 5-8 shows the simplified equation which relates iron release to the hydraulic residence time and geometric properties of the pipe.

$$\Delta Fe = \frac{Km \times HRT}{4 \times D} \tag{5-8}$$

Where:

ΔFe is the change in iron concentration as it passes through the pipe (mg/L)

Km is the iron flux (mg of iron/meter^2–day)

HRT is the hydraulic residence time (days)

D is the diameter of the pipe (meters)

The model was fitted by empirical data from experiments performed at variant hydraulic conditions on cast iron and galvanized pipe. Steady state conditions were defined after the effects of HRT on effluent turbidity were studied. Results showed that the iron flux under laminar flow conditions (Reynolds Numbers < 2000) was approximately constant for a given water quality. The reported average flux values were 1.99 mg Fe/m^2-day for galvanized steel, and 4.16 mg Fe/m^2-day for unlined cast iron pipe. The flux models developed for turbulent conditions (Re >2000) are shown in Equations 5-9 and 5-10. The complete calibration of the model at laminar and turbulent conditions is shown in Figure 5-1.

$$Galvanized\ Pipe: \quad Km = 4.5\times10^{-3}(\mathrm{Re}-2000)+1.99 \tag{5-9}$$

$$Cast\ Iron\ Pipe: \quad Km = 9.0\times10^{-3}(\mathrm{Re}-2000)+4.16 \tag{5-10}$$

Where:

Km is the iron flux (mg iron/m^2-day)

Re is the Reynolds Number, calculated by Equation 5-11:

$$\mathrm{Re} = \frac{DV}{\nu} \tag{5-11}$$

Where:

D is the pipe diameter (m)

V is the flow velocity (m/sec)

ν is the kinematic viscosity (m^2/sec)

ν can be assumed to be $1x10^{-6}$ m^2/sec at ambient temperatures near 20°C

This model was based on a constant water quality comprised of 60% groundwater, 30% surface water and 10% desalinated water. The flux model was adapted to predict flux under variant water quality conditions by incorporating the Imran et al. (2005) color release model. The adjustment term relates the predicted color of the influent water quality to the predicted water quality of the blend used during the experiments. Equation 5-12 shows the flux term being adjusted for water quality (Km_{adj}) by a predicted color ratio.

$$Km_{adj} = Km \times \frac{\Delta C_1}{\Delta C_2} \tag{5-12}$$

Where:

Km is the flux value

ΔC_1 is the predicted color of the influent water quality

ΔC_2 is the predicted color of the blend used for experiments

5.4 Methods and Materials

The pilot distribution system used for this analysis is the same used for the original flux model development. The site is located at the Cypress Creek Treatment Facility in Land O' Lakes, FL. The PDS construction remained unchanged from the previous study. The data used for this analysis comes from PDS 15, which was constructed of unlined cast

iron pipe, and PDS 18 which was constructed of galvanized pipe. The current iron release study was performed in conjunction with chlorine residual studies, which did not allow for complete independence of experimental design. An illustration of the PDS construction is shown in Figure 5-2.

5.4.1 Site Description

Four pilot distribution systems (PDS 15-18) were constructed from segments of cast iron (CI), lined cast iron (LCI), polyvinyl chloride (PVC) and galvanized steel (G) sections. The LCI (PDS 16) and PVC lines (PDS 17) were not used for this study due to previous results showing their negligible iron release. All pipe materials used in construction came from actual distribution systems serving the Tampa Bay area. Sample ports between each pipe length allowed for internal sampling. The approximate lengths of each pipe section in PDS 15 and PDS 18 are displayed in Table 5-1.

5.4.2 PDS Operation

Treated groundwater and desalinated water was used for these experiments. Batches of each source waters were prepared weekly following the treatment methods shown in Table 5-2. Source waters were allowed to equilibrate with the pipe materials for at least 3 days before sampling took place, which allowed for multiple flushes of the pipes. Experiments were conducted according to the schedule shown in Table 5-3. Influent flow was adjusted to match the targeted Reynolds number.

5.4.3 Sampling

Analysis from these sampling events was performed on the parameters shown in Table 5-4. Sampling was taken at the influent (I) and effluent (E) ports, with additional iron samples taken at varied internal sampling ports. The model developed by Mutoti et al. incorporated only influent and effluent sampling. Sample ports are described in Table 5-1 with the pipe lengths. Analysis followed a quality assurance-quality control (QA/QC) plan described in Table 5-5.

5.5 Results

5.5.1 Iron Flux Calculations

Experiments were performed in accordance to Table 5-3, with random sampling taken at intermediate ports between pipe lengths. Changes in iron concentrations were input into Equation 5-8 to calculate the iron flux (K_m), and then corrected using Equation 5-12 to adjust the flux value to the measured water quality. Appendix B contains the raw water quality data used to calculate the predicted delta color, the locations of each sampling, and the ratio of the predicted color of the current water quality to the water quality used to calibrate the original model.

5.5.2 Cast Iron Flux Results

The results of the cast iron experiments are shown in Table 5-6 as the weighted average flux values. Flux values were weighted by the by taking the proportion of the HRT between pipe sections to the total HRT (ratio of pipe lengths can also be used if the cross-sectional area is constant). Equation 5-13 shows the method of weighted average.

$$Weighted\ Average\ Flux = \frac{\sum_{I=1}^{N} (HRT\ Between\ Sections) \times (Km\ Between\ Sections)}{Total\ HRT} \quad (5\text{-}13)$$

For the cast iron PDS, the weighted flux values were considerably lower than predicted by the flux model. Using Equation 5-5, the water quality of the desalinated water (RO) typically predicted a color of 30-35, which would correspond to predicted color ratios of 3.5 to 4. These color ratios calculate to fluxes between 14 to 17 mg Fe/m^2-day. The actual iron flux calculations showed values between 5.5 to 8.25 mg Fe/m^2-day. The disagreement between the predicted and actual flux values is significant, as the predicted values are consistent in overpredicting the actual data. One experiment with groundwater was performed, which produced an iron flux of approximately 1 mg Fe/m^2-day. The predicted flux was approximately 2.7 mg Fe/m^2-day, which also showed a marked overprediction. These results can be compared to the original data by dividing the actual flux by the color ratio to normalize the water quality. Figure 5-3 shows the comparison of the original flux data to the new flux data after the actual results were normalized for water quality. These results also show consistently lower fluxes than the previous experiments.

These errors may have resulted from improper assumptions of steady state in the original model development. Figure 5-4 shows a typical time response curve for the release of turbidity during the original experiments. The graph shows that steady state release could be assumed to be reached at 3 pipe volumes. Due to water supply limitations, data could not be collected to see the effects after this point. Even though the change in turbidity is

shown to level off at 3 pipe volumes, a true steady state may not have been reached. This point may only represent a pseudo-steady state, and that over a longer period of time the turbidity release from the pipe would have reduced to an actual steady state value. Current experiments allowed many days for the pipes to equilibrate with the flow conditions, which better approximated a steady state iron release.

The averaged flux values with RO water quality ranged from approximately 5.5 to 8.25 mg Fe/m^2-day, which shows a flux that remained fairly constant despite slight water quality changes between experiments. Even though the weighted average flux values were nearly constant, the flux was more variant between sample ports. Appendix B shows that the iron release between sampling ports was not always constant as samples were typically taken between 2 or 3 sections of pipe. This is due in part to differences in the corrosion of each specific pipe section, as each pipe section is unique in its condition and placement. Over a long stretch of pipe, the differences could be assumed to average out to give a near constant flux, which is why the fluxes calculated by Mutoti et al. show less variation.

5.5.3 Re-evaluation of the Empirical Model Development

Upon closer examination of the raw data from the original model calibration, the constant flux for cast iron under near stagnant conditions may not be as high as the reported value for laminar conditions of 4.16 mg Fe/m^2-day. Table 5-7 shows the original flux calculations by Mutoti during the laminar experiments on cast iron pipe. At Reynolds Numbers less than 250, the original experiments seem to have an average flux less than 3

mg Fe/m^2-day. The flux values thereafter seem to have a slight rise between Reynolds Numbers of 250-2000. After analyzing the data, the results seem to support a piecewise model that incorporates near stagnant, upper laminar, and turbulent flow relationships.

Using the current and original flux data, a new modification to the original flux model was developed to explain the differences data at low and high laminar regions. The approximate average flux of the original and current data for Reynolds numbers less than 250 was 2.5 mg/meter^2-day. Flux values at Reynolds Numbers between 250 and 2000 (the laminar cut-off point) were better described by a linearly increasing trend. Linear regressions of the flux data at Reynolds Numbers between 250-2000 were used to develop an equation that appropriately described the data. The resulting equation changed the originally reported average flux at a Reynolds Number of 2000 from 4.16 mg/meter^2-day to approximately 10 mg/meter^2-day. The equation for the flux at turbulent conditions was adjusted to reflect the new flux at the laminar cut-off point. The new 3-piece flux equation is shown in Equations 5-14 to 5-16. The new model shown in Figure 5-5 shows an improvement in fit, especially in the new upper laminar region.

For Re < 250 (Near Stagnant):

$$Km = 2.5 \tag{5-14}$$

For 250 < Re < 2000 (Upper Laminar):

$$Km = 4.3 \times 10^{-3} (\mathrm{Re} - 250) + 2.5 \tag{5-15}$$

For Re > 2000 (Turbulent Flow):

$$Km = 9.0 \times 10^{-3} (\mathrm{Re} - 2000) + 10 \tag{5-16}$$

Where *Km* is in mg/meter^2-day

5.5.4 Galvanized Iron Flux Results

The experiments on the galvanized line were much less consistent and are summarized in Table 5-8. The same procedure was used for the galvanized flux calculations, but the values were calculated using the specific galvanized flux and predicted color equation shown in Equation 5-6. Problems resulted from the initial calculations which showed that the color release of desalinated water was approximately 1 CPU for the galvanized pipe. The color prediction for the galvanized model significantly differed from the color release model for cast iron pipe, which predicted colors of 30-35 CPU. Flaws in the galvanized model are believed to be due to the high dependence of the model on sulfate concentrations. The galvanized model was developed from a much more limited range of data than the cast iron predicted color model, and correspondingly could not accurately account for low sulfate concentrations. Table 5-9 shows the range of water quality variables used to construct the galvanized predicted color model. No sulfate concentrations less than 50 mg/L were experienced, while the RO water used in this study typically had a sulfate concentration less than 5 mg/L. These low predicted color values reduced the color ratio, and resulted in consistent underprediction of flux values. Predicted color values were also low in the groundwater as sulfate concentrations were only approximately 30 mg/L, although the color release would be expected to be low due to the high alkalinity.

Table 5-8 shows the flux values calculated using the galvanized color prediction model were at or less than 1 mg Fe/m^2-day, which is a very small number. Actual average flux values for RO water quality ranged from 6 to 10 mg Fe/m^2-day, and one experiment using GW resulted in an average flux of approximately 4 mg Fe/m^2-day. It became very apparent that the need for recalibration of the galvanized color release model was necessary to account for low sulfate concentrations and possibly the effects of water quality variables (such as HRT) that were originally excluded.

5.5.5 New Galvanized Model Development

The current experiments revealed the inadequacy of the galvanized color release model to predict color from low sulfate waters. Upon further examination into the data, it was discovered that the database used to construct the galvanized model was very limited in the range of most water quality variables. The entire database was constructed using only two blend compositions, and no data was collected using a singular source water. To expand this database, the data generated from both TBWI and TBWII projects were used to reformulate a new model that would have a larger range of application. The new database incorporated experiments using groundwater, desalinated water, and blend waters. The data set from the original TBWI project was condensed into 8 points which represented approximate 6 week averages. The averaging was necessary in order to relate the much larger TBWI database to the limited number of experiments performed in the TBWII study. This resulted in a total database of 12 individual points, which account for a larger range of water quality parameters but a smaller database size.

5.5.6 New Model Development Procedures

The traditional modeling procedure on the TBW projects uses an analysis of variance (ANOVA) test that excludes variables based on a 95% confidence limit. All of the water quality parameters are treated as variables and are eliminated by removing the least significant variable in successive trials until the remaining variables satisfy the 95% limit. With only 12 points in the data set, the entire set of water quality parameters was not able to be used as the number of variables would outnumber the number of independent observations. Six water quality parameters (hydraulic residence time, sulfates, chlorides, alkalinity, temperature and dissolved oxygen) were selected to be used in the initial modeling attempts due to their reported influence in affecting iron release. The combined database used for the new model development is shown in Table 5-10. The level of significance was also relaxed from 95% to 75% so that a reasonable number of parameters would stay in the model. The results of the new modeling attempt yielded the following equation:

$$\Delta Fe = \frac{.395 \times (HRT)^{0.17} \times (Cl^-)^{0.72} \times (1.45)^{T/25}}{(ALK)^{0.97}}$$

Where:

Fe is the iron concentration (mg/L)

HRT is the hydraulic residence time (days)

Cl^- is the chloride concentration (mg/L)

T is the temperature (^oC)

ALK is the alkalinity (as mg/L $CaCO_3$)

The new model exhibits a good fit with the combined data set and is shown in Figure 5-6. The model was also examined using a sensitivity analysis. The results showed that the typical desalinated water quality would result in the highest iron release, while the groundwater would result in the lowest iron release. These findings concur with the results from the experiments using cast iron pipe. The model may be limited by a small database, but it offers an improvement over the original galvanized model. It is cautioned that a more thorough database would be needed to better calibrate the determined constant values.

5.5.7 Calculations of Galvanized Iron Flux Using New Model

Using the new model, the galvanized flux results were recalculated using a ratio of the predicted iron release of the current water quality to the predicted iron release of the blend used in the previous experiments. Using this procedure is not an independent analysis, as the some of the data used to construct the new model comes from the current experiments. The predicted iron release using the new model of the blend used for the original experiments at a 5-day HRT and 20^{o}C temperature is approximately 0.08 mg/L. Using this value, the predicted iron release for each of the current experiments was recalculated with the new model and used to determine new flux values. The results in Table 5-11 show the great improvement the new model offers over the old model. The error in predictions reduced dramatically for each experiment, and the results are more reasonable. The predictions using RO only showed a moderate prediction error of

approximately 5-25%. The GW experiment was still underpredicted by over 50%, but the new results show a definite improvement.

5.6 Conclusions and Recommendations

This limited study sought to evaluate the novel iron flux model developed by Mutoti. The current results show an overprediction of iron flux when desalinated water was fed into the cast iron pipe. An experiment using groundwater also resulted in overprediction of the actual data. Possible flaws with the empirical calibration of the original model could be due to an error in assuming steady-state conditions. Steady-state iron release was assumed to be reached after 3 pipe volumes had passed through the system. This assumption was based on experiments that showed the turbidity release from the cast iron pipe was nearly constant at this time. Limited water quantities prohibited the evaluation of these conclusions over many pipe volumes. The current experiments allowed for longer stabilization times, in which the water was flushed though the pipes for many days. The pseudo-steady state reached during the original model development was probably not the true steady state iron release from the pipe. Most likely the stabilization would take many pipe volumes and the results of the present experiments more closely resemble steady state.

A more detailed analysis of the original data showed that the assumed laminar average of 4.16 mg/m^2-day may not be appropriate for the low laminar range. For Reynolds Numbers at near stagnant conditions ($Re < 250$), the average of the current and original experiments was approximately 2.5 mg/m^2-day. A proposed change to the upper laminar

region (Re > 250) would show a slight linear increase between Reynolds numbers of 250 and 2000. While the equation for turbulent flow was adjusted to intersect with the new upper laminar region at the laminar cut off point (Re = 2000).

The galvanized experiments showed a consistent underprediction, mostly due to the inadequacy of the galvanized color release model. Values calculated for the predicted color release from the galvanized model were not reasonable for waters with low sulfate concentrations. A new galvanized model was created by combining data from the original and current studies. The new model returned more reasonable predicted color values when desalinated water quality was used. The new model was used to recalculate the iron flux for the current experiments. The new calculated flux offered a great improvement over the original predicted flux values. The new model is limited by the small database and the lack of independent testing, but offers signifcantly improved results over the original model.

The results from both experiments show a fairly consistent average flux under different laminar flows. Internal sampling between pipe lengths showed that the flux is not truly constant, but can be averaged to approximate a near constant value in long sections of pipe. The recalibration of the cast iron flux model under laminar flow conditions resulted in a better fit to the combined data of original and current experiments, but a more thorough analysis at the upper laminar and turbulent regions would be needed to validate the newly proposed model changes. The new galvanized model would also need an

expanded database to improve the calibration. An extensive study of different influent water qualities at different HRT would be needed to verify the new galvanized model.

5.7 Acknowledgment

The authors wish to acknowledge Chris Owen, Tampa Bay Water Authority Quality Assurance Officer, who was the TBW Project Coordinator, and Roy Martinez, AWWA Research Foundation Senior Account Officer, who was the AwwaRF Project Officer, and the following Member Governments: Pinellas County, Hillsborough County, Pasco County, Tampa, St. Petersburg, and New Port Richey. Pick Talley, Robert Powell, Dennis Marshall and Oz Wiesner from Pinellas County, and Dr. Luke Mulford from Hillsborough County are also specifically recognized for their contributions. Several UCF Environmental Engineering students and faculty also contributed significantly to this project and are recognized for their efforts.

5.8 Figures and Tables

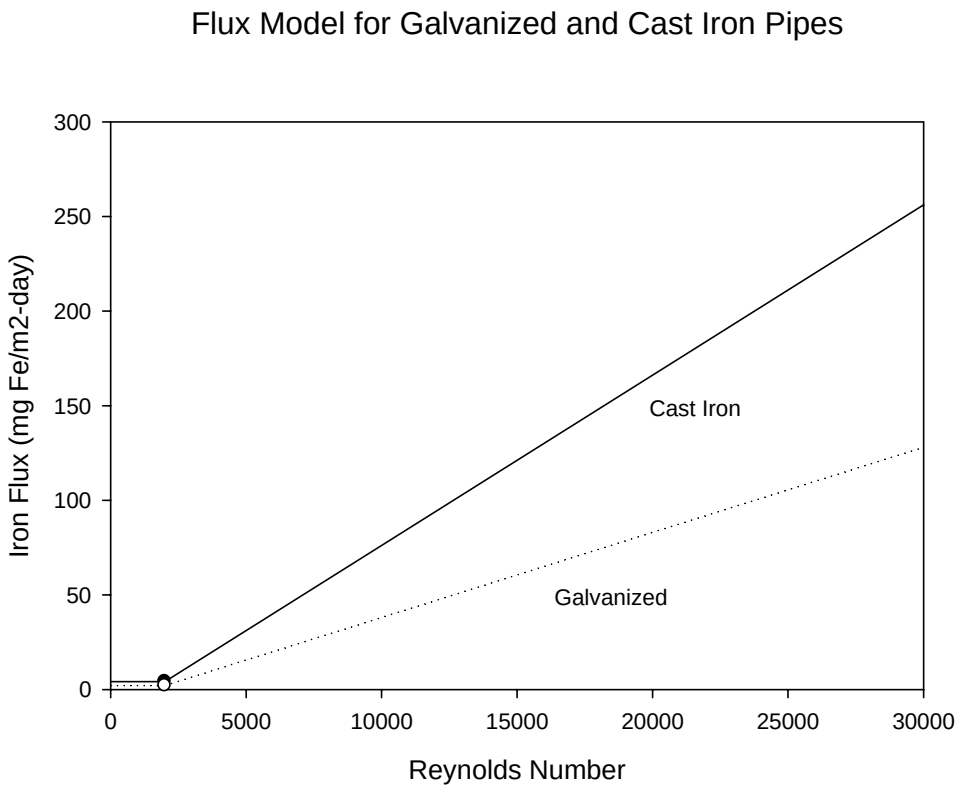


Figure 5-1: Flux Model for Galvanized and Cast Iron Pipes

Figure 5-2: PDS Construction

Table 5-1: PDS Pipe Lengths

Pipe #	PDS 15	PDS 18
1	12	13
2	12	15
3	12	13
4	12	21
5	11	25
6	11	7
7	10	20
8	11	20
9	--	10

* all lengths are in units of feet (no 9th section in PDS 15)

Table 5-2: Source Water Summary

Water Type	Treatment
Ground Water (GW)	Treatment by aeration, free chlorine, added ammonia to form combined chlorine.
Desalinated Water (RO)	Treatment by reverse osmosis membranes, aeration, disinfection by free chlorine, added ammonia to form combined chlorine, dissolved salt addition to simulate desalination process.

Table 5-3: Experimental Sample Plan

PDS	Re	Source Water
15	50	RO
15	100	RO
15	100	GW
15	200	RO
18	50	RO
18	100	RO
18	150	GW
18	200	RO

Table 5-4: Analysis Performed During Experiments

Parameter	Method of Quantification
Ammonia	Ammonia Probe
pH	pH Probe
Alkalinity	Titration
UV-254	Spectrophotometer
Dissolved Oxygen	Dissolved Oxygen Probe
Temperature	Dissolved Oxygen Probe
Silica	Spectrophotometer/ICP
Total Chlorine	Spectrophotometer
Turbidity	Spectrophotometer
Apparent Color	Spectrophotometer
Conductivity	Conductivity Probe
Sodium	Spectrophotometer
Chloride	Titration/IC
Sulfate	Spectrophotometer/IC
Total Iron	Spectrophotometer/ICP

Table 5-5: QA/QC Plan

Parameter	Blanks (Every Sampling)	Standards (Every Sampling)	Duplicates (10% of Samples)	Spikes (10% of samples)
Ammonia	X	X	X	X
pH	X	X	X	
Alkalinity	X	X	X	X
UV-254	X		X	
Dissolved Oxygen			X	
Temperature				
Silica	X	X	X	X
Total Chlorine	X	X	X	
Turbidity	X	X	X	
Apparent Color	X	X	X	
Conductivity	X	X	X	
Sodium	X	X	X	X
Chloride	X	X	X	X
Sulfate	X	X	X	X
Total Iron	X	X	X	X

Table 5-6: Results of Cast Iron Flux Experiments

Reynolds Number	Source Water	Total HRT (hr)	Average Weighted Flux (mg Fe/m^2-day)	Predicted Color (CPU)	Predicted Color Ratio	Predicted Flux (mg Fe/m^2-day)
50	RO	23	5.5	35.9	4.1	17.0
100	RO	11.6	8.3	30.1	3.4	14.2
150	RO	7.8	6.5	31.1	3.5	14.7
100	GW	11.6	1.0	5.7	0.65	2.7

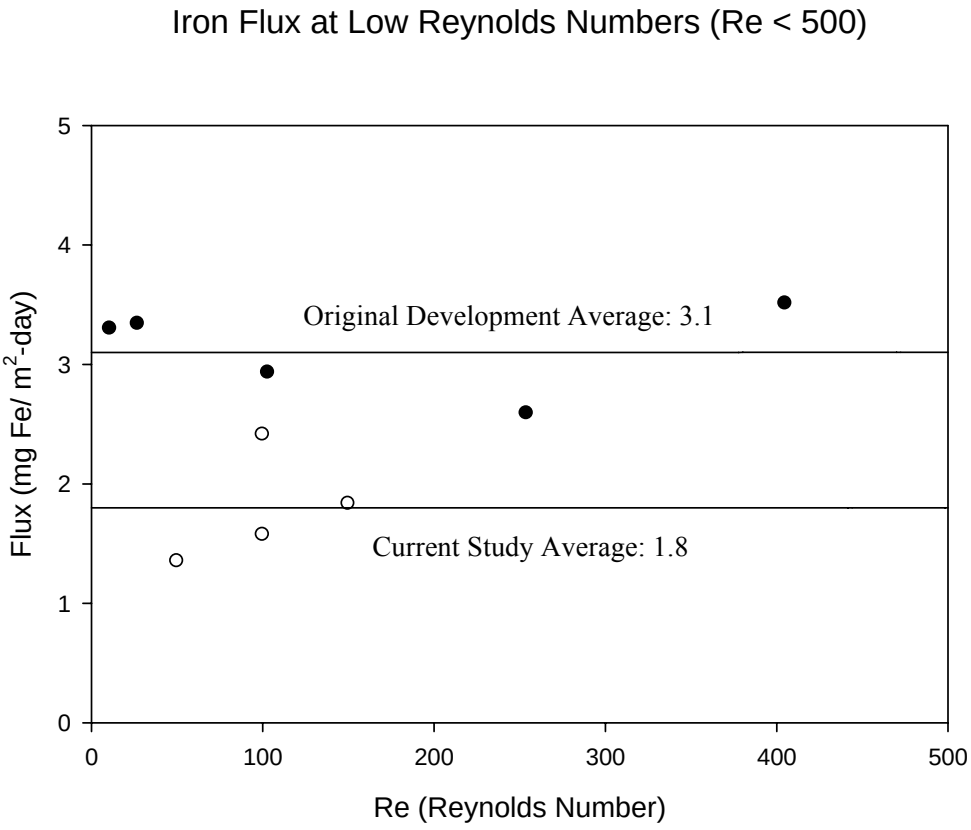
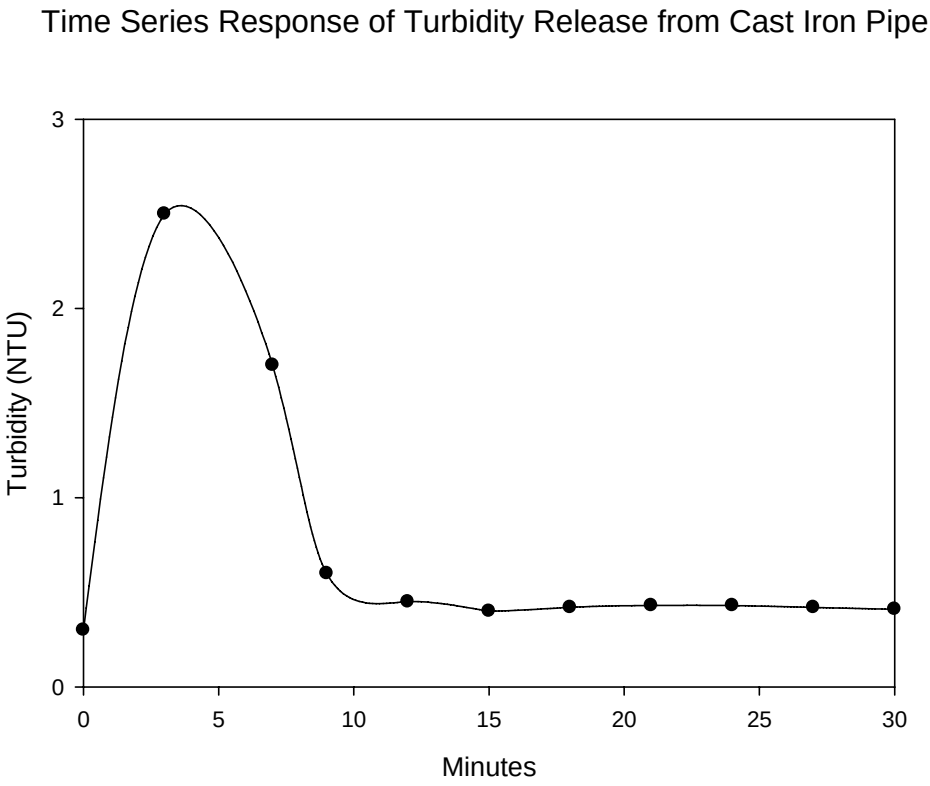


Figure 5-3: Flux as a Function of Reynolds Number



(Re = 10311, HRT = 6.6 minutes)

Figure 5-4: Time Response Curve for Assumption of Steady State Release (Mutoti 2007)

Table 5-7: Original Flux Values by Mutoti During Laminar Conditions

Re	**Flux (mg/m^2-day)**
10.8	3.3
27	3.3
103	2.9
254	2.6
405	3.5
794	12.4
1161	6.8
1253	2.8
1566	7.2
1674	9.9
2019	3.6

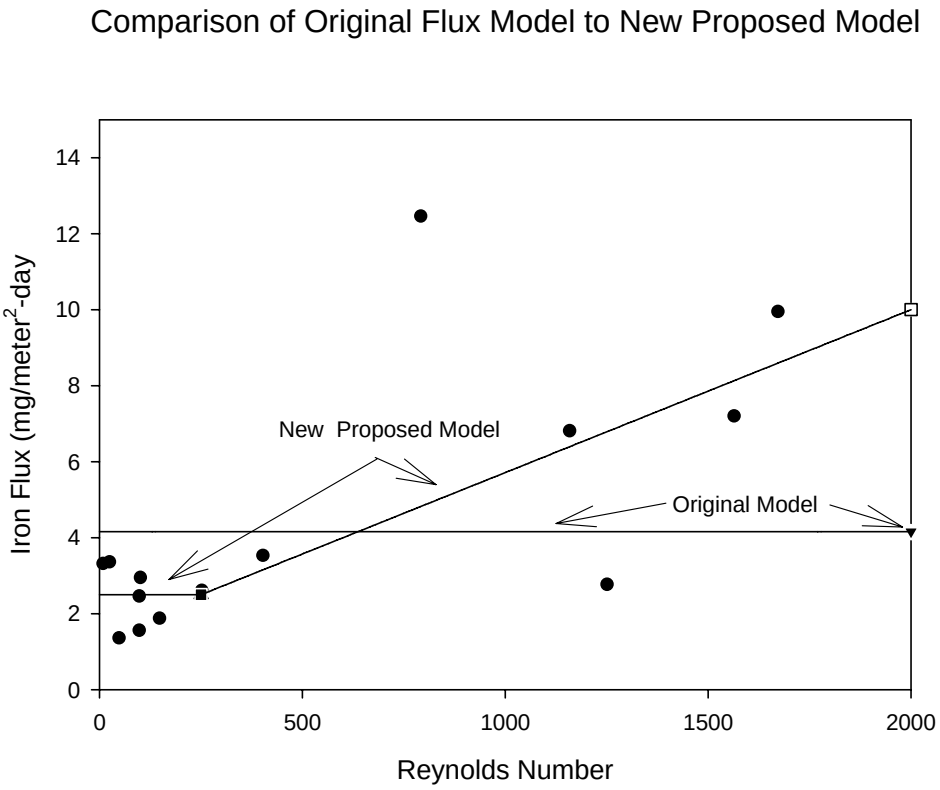


Figure 5-5: Comparison of New Model to Original Model

Table 5-8: Results of Galvanized Flux Experiments

Reynolds Number	Source Water	Total HRT (hr)	Average Weighted Flux (mg Fe/m^2-day)	Predicted Color (CPU)	Predicted Color Ratio	Predicted Flux (mg Fe/m^2-day)
50	RO	12.3	6.3	1.3	0.5	1.0
100	RO	6.1	9.9	1.1	0.4	0.8
150	GW	4.1	4.5	0.5	0.2	0.4
200	RO	2.7	8.4	0.7	0.26	0.5

Table 5-9: Range of Water Quality used for Development of the Original Galvanized Color Release Model

Parameter	Minimum	Maximum	Average
Alkalinity (mg/L as CaCO3)	92	200	126
Sulfate (mg/L)	59	102	86
Silica (mg/L as SiO2)	3	14	8
Temperature (oC)	14.5	28.6	22.6

Table 5-10: Data Used for New Galvanized Model Development

Δ Fe (mg/L)	HRT (days)	Sulfates (mg/L)	Chlorides (mg/L)	Alkalinity (mg/L $CaCO_3$)	Temperature (oC)
0.15	5	130	64	103	16
0.16	5	120	57	99	18
0.11	5	105	43	130	23
0.13	5	95	40	142	25
0.06	5	80	59	108	27
0.12	2	70	50	111	28
0.14	2	95	40	90	25
0.12	2	100	45	75	19
0.25	0.5	5	95	73	26
0.2	0.25	4	108	71	24
0.03	0.17	30	44	220	25
0.08	0.12	3	79	74	20

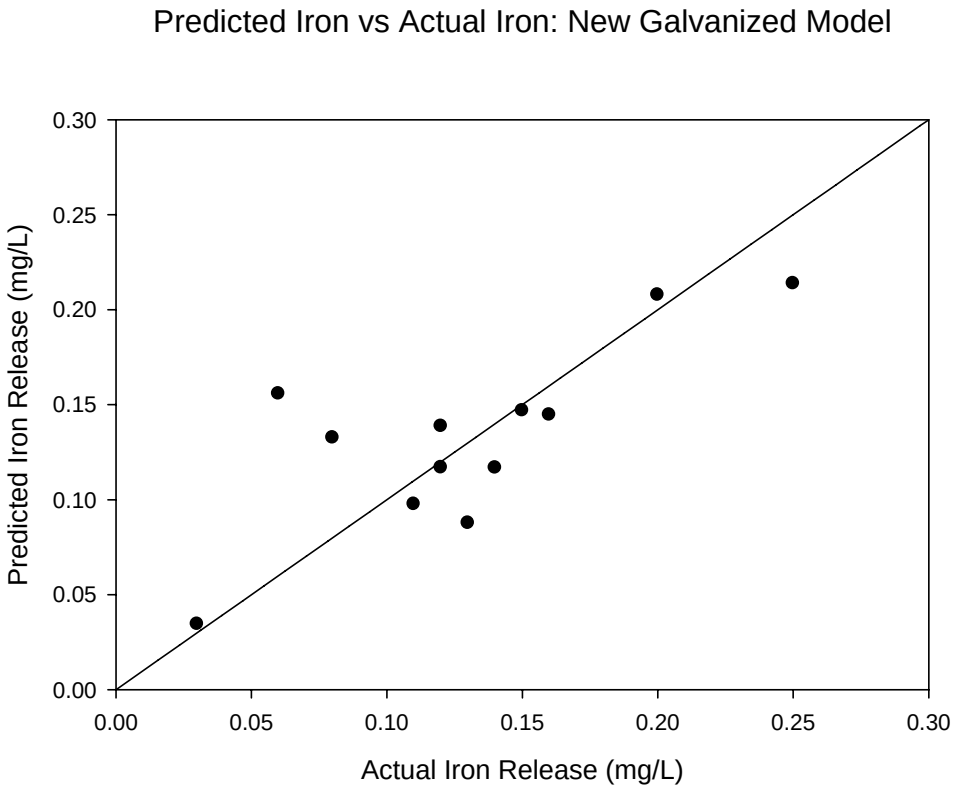


Figure 5-6: Predicted Versus Actual Iron Release for New Galvanized Model

Table 5-11: Flux Calculations Using New Galvanized Model

Reynolds Number	Source Water	Total HRT (hr)	Average Weighted Flux (mg Fe/m^2-day)	Predicted Iron (mg/L)	Predicted Iron Ratio	Predicted Flux (mg Fe/m^2-day)
50	RO	12.3	6.3	0.32	4.2	8.4
100	RO	6.1	9.9	0.35	4.6	9.3
150	GW	4.1	4.5	0.06	0.8	1.6
200	RO	2.7	8.4	0.25	3.3	6.5

5.9 References

1. Butler, G. & Ison, H., 1966. *Corrosion and its Prevention in Waters*. Reinhold Publishing, New York.
2. Costello, J., 1984. Postprecipitation in Distribution Systems. *Jour. AWWA,* 76:11:46
3. Curry, M., 1978. Is Your Water Safe and What Difference Does It Make. *Jour. AWWA*, 70:9:506
4. Edwards, M.; Schock, M.; & Meyer, T., 1996. Alkalinity, pH and Copper Corrosion By-product Release. *Jour. AWWA,* 88:3:81.
5. Holler, A., 1978. Corrosion of Water Pipes *Jour. AWWA*, 70:8:456.
6. Imran, S. et al., 2005. Red Water Release in Drinking Water Distribution Systems. *Jour. AWWA*, 97:9:93.
7. Kirmeyer, G. & Logsdon, G., 1983. Principles of Internal Corrosion and Corrosion Monitoring. *Jour. AWWA*, 75:2:78
8. Langelier, W., 1936. The Analytical Control of Anti-Corrosion Water Treatment *Jour. AWWA,* 28:10:1500.
9. Larson, T. & Skold, R., 1958. Laboratory Studies Relating Mineral Water Quality of Water to Corrosion of Steel and Cast Iron. *Corrosion,* 14:6:43.
10. McNeill, L. & Edwards, M., 2001. Iron Pipe Corrosion in Distribution Systems. *Jour. AWWA*, 93:7:93.
11. Mullen E. and Ritter J., 1980. Monitoring and Controlling Corrosion by Potable Water *Jour. AWWA,* 72:5:286.

12. Mutoti, G. et al., 2007a. Development of a Novel Iron Release Flux Model for Distribution Systems. *Jour. AWWA*, 99:1:102.

13. Mutoti, G. et al., 2007b. Pilot Scale Verification and Analysis of Iron Release Flux Model. *Jour. Environ. Eng.*, 133:2:173-179.

14. Pisigan R. and Singley J., 1985. Effects of Water Quality Parameters on the Corrosion of Galvanized Steel. *Jour AWWA,* 77:11:76.

15. Rossum, J. & Merrill, T., 1983. An Evaluation of the Calcium Carbonate Saturation Indexes. *Jour. AWWA,* 75:2:96.

16. Shull, K., 1980. An Experimental Approach to Corrosion Control. *Jour. AWWA*, 72:5:280.

17. USEPA, 2003. *National Primary Drinking Water Standards*, Washington, D.C.

18. Volk, C.; Dundore, E.; Schiermann, J.; & LeChevallier M., 2000 Practical Evaluation of Iron Corrosion Control in a Drinking Water Distribution System. *Wat. Res.*, 34:6:1967.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Verification of a Non-Linear Color Release Model

The results of the study of PDS 13 and PDS 14 revealed the average iron concentration was significantly greater in PDS 13, with a much greater tendency to exceed the secondary standard. The historical non-linear color release developed by Imran was valid in predicting color release in PDS 14, but not in PDS 13. The corresponding increase in color and iron from PDS 13 were fairly well described by the Modified Larson Ratio, but not by LSI.

A general trend of decreasing iron with increasing LSI was observed, but relatively high iron values still occurred at high influent LSI values. Based on this research, it was seen that other water quality parameters outside of the LSI had better correlations with iron release. Therefore, it is cautioned that LSI is not suitable as a universal predictor of iron release. An attempt to model the data with a new non-linear power model resulted in only slightly better results than the MLR and incorporated the same parameters already accounted for in the MLR equation. An analysis of variance test at the 95% significance level showed that the pH, LSI, and pHs were insignificant variables in separate model developments. Imran's color release model is recommended under similar well-

stabilized conditions used to develop the model, while MLR is recommended as a better predictor of iron release under more aggressive conditions.

Due to the limitations of this study, a full study of the effects pH and LSI have on iron release were unable to be performed. Other methods of raising and lowering pH, such as recarbonation with lime, would need to be investigated to fully separate the effects of water quality from pH and LSI. The effects of water quality were only evaluated under a somewhat small range and the hydraulic effects were not examined.

6.2 Verification of a Novel Iron Release Flux Model

This limited study sought to evaluate the novel iron flux model developed by Mutoti. The results show an overprediction of iron release for cast iron pipe with desalinated water. Experimental flux values were 50%-75% less than the predicted values. The model was developed based on assumed steady-state conditions. These steady state conditions were assumed to exist after passage of 3 pipe volumes, based on an experiment that showed the turbidity release from the cast iron pipe was constant at this time. Limited water quantities prohibited full evaluation of these conclusions. The current experiments allowed for longer stabilization times, where water was flushed though the pipes for many days. The pseudo-steady state reached during the original model development was likely not the true iron release from the pipe. It is likely that stabilization would require additional water volumes so that the results of the current experiments more closely resemble steady state.

Additional investigation into the original model development revealed that the assumption of a constant flux for all laminar flow may be invalid. Experiments at near stagnant conditions showed a smaller average flux than the average flux for other laminar conditions. The flux values for Reynolds Numbers less than 250 for the current and original experiments showed an average of approximately 2.5 mg/m^2-day. A slight linear increase was also proposed between Re of 250 and 2000 based on a closer inspection of the original data. More data in the upper laminar range would help to verify the newly developed model.

The galvanized experiments showed a marked overprediction to the predicted values, mostly due to the inadequacy of the galvanized color release model. Values calculated for the predicted color release from the galvanized model were not able to account for the low sulfate concentrations experienced in the current study. A new galvanized model was developed from a combination of the new and original data that improved flux predictions. This model was developed using a limited database and was not able to be independently tested.

APPENDIX A: VERIFICATION OF A NON-LINEAR COLOR MODEL

Table A-1: Average Water Quality for PDS 13 and PDS 14

Parameter	**PDS 13**	**PDS 14**
Delta Iron (mg/L)	0.147	0.083
Delta Turbidity (NTU)	0.768	0.291
Delta Color (CPU)	14	7
Predicted Color (CPU)	10	8
pH (Units)	7.74	7.97
LSI (Units)	0.28	0.56
Sodium (mg/L)	32	28
Chlorides (mg/L)	75	57
Sulfates (mg/L)	74	75
Alkalinity (mg/L as $CaCO_3$)	130	139
Dissolved Oxygen (mg/L)	8.34	8.27
Temperature (^oC)	23.2	23.5
Calcium (mg/L)	70	72
Magnesium (mg/L)	7	7
Total Chlorine (mg/L as Cl_2)	4.6	5.1
Silica (mg/L as SiO_2)	8.4	8.5
Modified Larson Ratio (Units)	0.21	0.18

Table A-2: Minimum and Maximum Values from PDS 13 and PDS 14

Parameter	Minimum Values		Maximum Values	
	PDS 13	**PDS 14**	**PDS 13**	**PDS 14**
Delta Iron (mg/L)	0.002	0.000	0.466	0.180
Delta Turbidity (NTU)	0.222	0.065	2.122	0.696
Delta Color (CPU)	1	0	53	20
Predicted Color (CPU)	2	2	24	15
pH (Units)	7.43	7.57	8.20	8.36
LSI (Units)	-0.14	0.11	0.78	1.07
Sodium (mg/L)	6	5	73	92
Chlorides (mg/L)	38	38	123	79
Sulfates (mg/L)	54	54	105	115
Alkalinity (mg/L as $CaCO_3$)	84	98	168	169
Dissolved Oxygen (mg/L)	6.72	6.58	10.90	10.70
Temperature (^oC)	11.8	11.3	29.7	29.0
Calcium (mg/L)	47	50	88	84
Magnesium (mg/L)	6	6	8	8
Total Chlorine (mg/L as Cl_2)	3.0	2.8	6.7	6.8
Silica (mg/L as SiO_2)	4.4	4.0	13.6	13.4
Modified Larson Ratio (Units)	0.06	0.06	0.42	0.34

Table A-3: Water Quality Summary for Development of TBWI Hybrid PDS Color Release Model

Parameter	**Minimum**	**Maximum**	**Average**
Alkalinity (mg/L as $CaCO_3$)	51	210	106
Calcium (mg/L)	23	88	50
Chlorides (mg/L)	19	100	46
Sulfate (mg/L)	4	232	60
Sodium (mg/L)	12	65	35
Silica (mg/L as SiO_2)	1	16	10
Dissolved Oxygen (mg/L)	6.9	12.2	8.3
Conductivity (μS/cm)	331	707	489
pH (Units)	7.8	8.4	8.1
Temperature (^oC)	16.8	27	23.5

Table A-4: Correlations Between Water Quality Parameters and Color, Turbidity, and Iron Release for PDS 13

Parameter	Delta Color	Delta Turbidity	Delta Iron
pH	--	--	--
pHs	--	0.1	--
LSI	--	--	--
Alkalinity	0.34	0.6	0.16
Chlorides	--	0.11	0.22
Sodium	0.18	0.21	0.36
Sulfate	0.27	0.5	0.25
Temperature	0.26	0.27	--
Dissolved Oxygen	0.26	0.31	0.14
Calcium	--	--	--
Conductivity	--	--	--
Silica	0.22	0.31	0.21
Larson Ratio	0.27	0.6	0.31
Modified Larson Ratio	0.41	0.7	0.26

*Number Denotes Regression Coefficient (R^2)
-- Represents Poor Correlation ($R^2 < 0.1$)

APPENDIX B: VERIFICATION OF A NOVEL IRON FLUX MODEL

Table B-1: Water Quality Summary for Development of TBWI Galvanized PDS Color Release Model

Parameter	**Minimum**	**Maximum**	**Average**
Alkalinity (mg/L as CaCO3)	92	200	126
Chlorides (mg/L)	35	66	48
Sulfate (mg/L)	59	102	86
Sodium (mg/L)	28	85	46
Silica (mg/L as SiO2)	3	14	8
Dissolved Oxygen (mg/L)	6.5	8.4	8.2
pH (Units)	7.8	8.2	8
Temperature (oC)	14.5	28.6	22.6

Table B-2: Raw Data Collected for Galvanized Flux Model Testing: RO Influent at a Reynolds Number of 50 (121 mL/min)

Date	PDS	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	Temp. (oC)	Alk (mg/L CaCO3)	SO4 (mg/L)	SiO2 (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
7/27/2006	18	0 (Influent)	0	0.0	0.033	26.5	73	5	2	1.3	0.487
7/27/2006		1	13	1.1	0.133						
7/27/2006		2	15	1.3	0.160						
7/27/2006		3	13	1.1	0.206						
7/27/2006		4	21	1.8	0.251						
7/27/2006		5	25	2.1	0.276						
7/27/2006		6	7	0.6	0.258						
7/27/2006		7	20	1.7	0.276						
7/27/2006		8	20	1.7	0.283						
7/27/2006		9 (Effluent)	10	0.9	0.285						

Table B-3: Raw Data Collected for Galvanized Flux Model Testing: RO Influent at a Reynolds Number of 100 (242 mL/min)

Date	PDS	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	Temp. (oC)	Alk (mg/L CaCO3)	SO4 (mg/L)	SiO2 (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
9/8/2006	18	0 (Influent)	0	0.0	0.010	24.8	71	3	1	1.1	0.392
9/8/2006		1	13	0.6							
9/8/2006		2	15	0.6							
9/8/2006		3	13	0.6	0.169						
9/8/2006		4	21	0.9							
9/8/2006		5	25	1.1							
9/8/2006		6	7	0.3							
9/8/2006		7	20	0.9	0.172						
9/8/2006		8	20	0.9							
9/8/2006		9 (Effluent)	10	0.4	0.209						

Table B-4: Raw Data Collected for Galvanized Flux Model Testing: GW Influent at a Reynolds Number of 150 (363 mL/min)

Date	PDS	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	Temp. (oC)	Alk (mg/L CaCO3)	SO4 (mg/L)	SiO2 (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
10/5/2006	18	0 (Influent)	0	0.0	0.081	25.5	221	28	12	0.5	0.197
10/5/2006		1	13	0.4	0.090						
10/5/2006		2	15	0.4							
10/5/2006		3	13	0.4	0.108						
10/5/2006		4	21	0.6							
10/5/2006		5	25	0.7	0.104						
10/5/2006		6	7	0.2							
10/5/2006		7	20	0.6	0.120						
10/5/2006		8	20	0.6							
10/5/2006		9 (Effluent)	10	0.3	0.102						

Table B-5: Raw Data Collected for Galvanized Flux Model Testing: RO Influent at a Reynolds Number of 200 (484 mL/min)

Date	PDS	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	Temp. (oC)	Alk (mg/L CaCO3)	SO4 (mg/L)	SiO2 (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
10/26/2006	18	0 (Influent)	0	0.0	0.039	19.1	74	4	2	0.7	0.262
10/26/2006		1	13	0.3							
10/26/2006		2	15	0.3							
10/26/2006		3	13	0.3							
10/26/2006		4	21	0.4							
10/26/2006		5	25	0.5	0.112						
10/26/2006		6	7	0.1							
10/26/2006		7	20	0.4							
10/26/2006		8	20	0.4							
10/26/2006		9 (Effluent)	10	0.2	0.112						

Table B-6: Raw Data Collected for Cast Iron Flux Model Testing: RO Influent at a Reynolds Number of 50 (363 mL/min)

Date	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	D.O. (mg/L)	Temp (^oC)	Alk (mg/L $CaCO_3$)	SO_4 (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
9/15/2006	0	0	0.0	0.011	7.47	26	71	3	108	48	35.9	4.075
9/15/2006	1	12	3.1									
9/15/2006	2	12	3.1									
9/15/2006	3	12	3.1	0.069								
9/15/2006	4	12	3.1									
9/15/2006	5	11	2.8									
9/15/2006	6	11	2.8	0.111								
9/15/2006	7	10	2.6									
9/15/2006	8	11	2.8	0.151								

Table B-7: Raw Data Collected for Cast Iron Flux Model Testing: RO Influent at a Reynolds Number of 100 (726 mL/min)

Date	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	D.O. (mg/L)	Temp (^{o}C)	Alk (mg/L $CaCO_3$)	SO_4 (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
9/22/2006	0	0	0.0	0.009	7.68	24.9	60	1	87	41	30.1	3.419
9/22/2006	1	12	1.5	0.067								
9/22/2006	2	12	1.5	0.065								
9/22/2006	3	12	1.5									
9/22/2006	4	12	1.5	0.098								
9/22/2006	5	11	1.4									
9/22/2006	6	11	1.4	0.104								
9/22/2006	7	10	1.3									
9/22/2006	8	11	1.4	0.114								

Table B-8: Raw Data Collected for Cast Iron Flux Model Testing: GW Influent at a Reynolds Number of 100 (726 mL/min)

Date	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	D.O. (mg/L)	Temp (^{o}C)	Alk (mg/L $CaCO_3$)	SO_4 (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
10/5/2006	0	0	0.0	0.081	7.35	26	221	28	44	16	5.7	0.649
10/5/2006	1	12	1.5	0.079								
10/5/2006	2	12	1.5									
10/5/2006	3	12	1.5	0.084								
10/5/2006	4	12	1.5									
10/5/2006	5	11	1.4									
10/5/2006	6	11	1.4									
10/5/2006	7	10	1.3									
10/5/2006	8	11	1.4	0.094								

Table B-9: Raw Data Collected for Cast Iron Flux Model Testing: RO Influent at a Reynolds Number of 150 (1089 mL/min)

Date	Sample Port	Pipe Length (ft)	HRT (Hrs)	Iron (mg/L)	D.O. (mg/L)	Temp (^{o}C)	Alk (mg/L $CaCO_3$)	SO_4 (mg/L)	Cl^- (mg/L)	Na^+ (mg/L)	Predicted ΔC	Color Ratio $\Delta C_2/\Delta C_1$
10/12/2006	0	0	0.0	0.006	7.96	24.7	75	4	98.5	40	31.1	3.539
10/12/2006	1	12	1.0	0.010								
10/12/2006	2	12	1.0									
10/12/2006	3	12	1.0	0.026								
10/12/2006	4	12	1.0									
10/12/2006	5	11	0.9									
10/12/2006	6	11	0.9									
10/12/2006	7	10	0.9									
10/12/2006	8	11	0.9	0.061								